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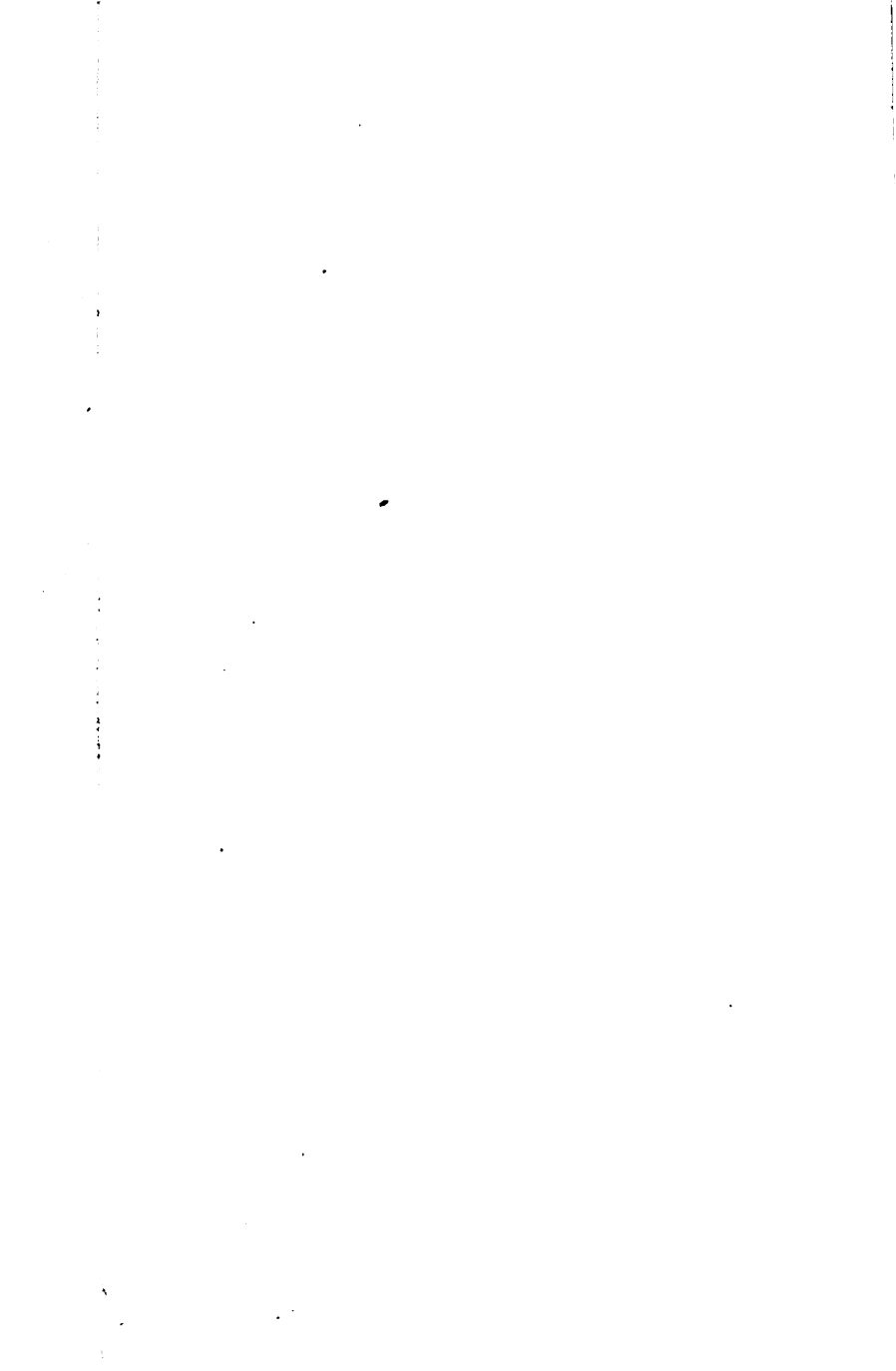
FIXATION OF ATMOSPHERIC NITROGEN

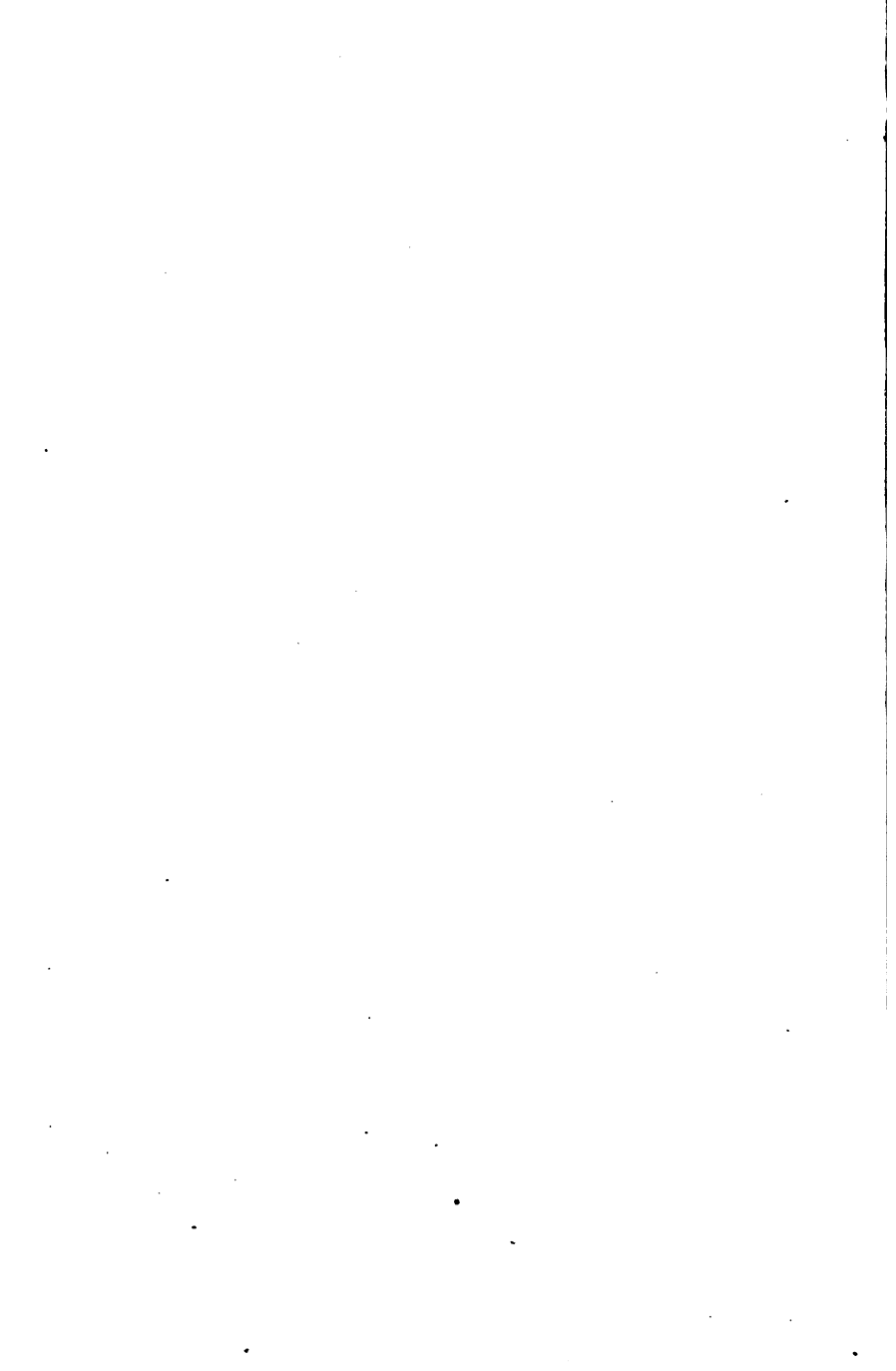
JOSEPH KNOX



D. Van Nostrand Company







CHEMICAL MONOGRAPHS

EDITED BY A. C. CUMMING, D.Sc.

No. IV

The Fixation of Atmospheric Nitrogen

CHEMICAL MONOGRAPHS

EDITED BY A. C. CUMMING, D.Sc.

THE progress of Chemistry is so rapid that it is becoming a matter of ever-increasing difficulty to keep abreast of the modern developments of the science. The volume of periodical literature is so enormous that few can hope to read, far less assimilate, all that is published. The preparation of summaries has therefore become a necessity, and has led to the publication of various well-known journals devoted to the abstraction of original papers. For obvious reasons, however, these do not fully supply the wants of advanced students and research workers, and it is now generally recognised that monographs on special subjects are also needed.

This series of monographs is intended primarily for Advanced and Honours students. As each monograph is written by an author with special knowledge of the subject, and copious references are given, it is hoped that the series will prove useful also to those engaged in research.

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THE FIXATION OF ATMOSPHERIC NITROGEN. By JOSEPH KNOX, D.Sc., Lecturer on Inorganic Chemistry, University of Aberdeen.

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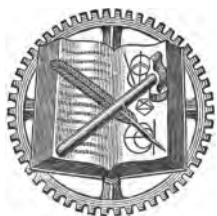
Other Volumes to follow.

The Fixation of Atmospheric Nitrogen

BY

JOSEPH KNOX, D.Sc.

Lecturer on Inorganic Chemistry, University of Aberdeen



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NEW YORK
D. VAN NOSTRAND COMPANY
TWENTY-FIVE PARK PLACE

1914

TP 245
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PREFACE

IN the following pages I have tried to give an account of the more important processes for the fixation of atmospheric nitrogen, and, more especially, of the theory on which they are based. No attempt has been made even to mention all the proposals regarding methods and apparatus to be found in the patent literature of recent years. The mere enumeration of these would almost occupy the space at my disposal, and in many cases there is no evidence that the proposed methods are in any way workable. I have, therefore, confined myself to those methods which are either in actual operation, or which show promise of assuming technical importance in the near future. I am indebted to the admirable consular report on *The Utilisation of Atmospheric Nitrogen*, by T. E. Norton, for some valuable information on the purely technical part of the subject. The report also contains an excellent account of the financial and commercial organisation of the various industries connected with the fixation of nitrogen.

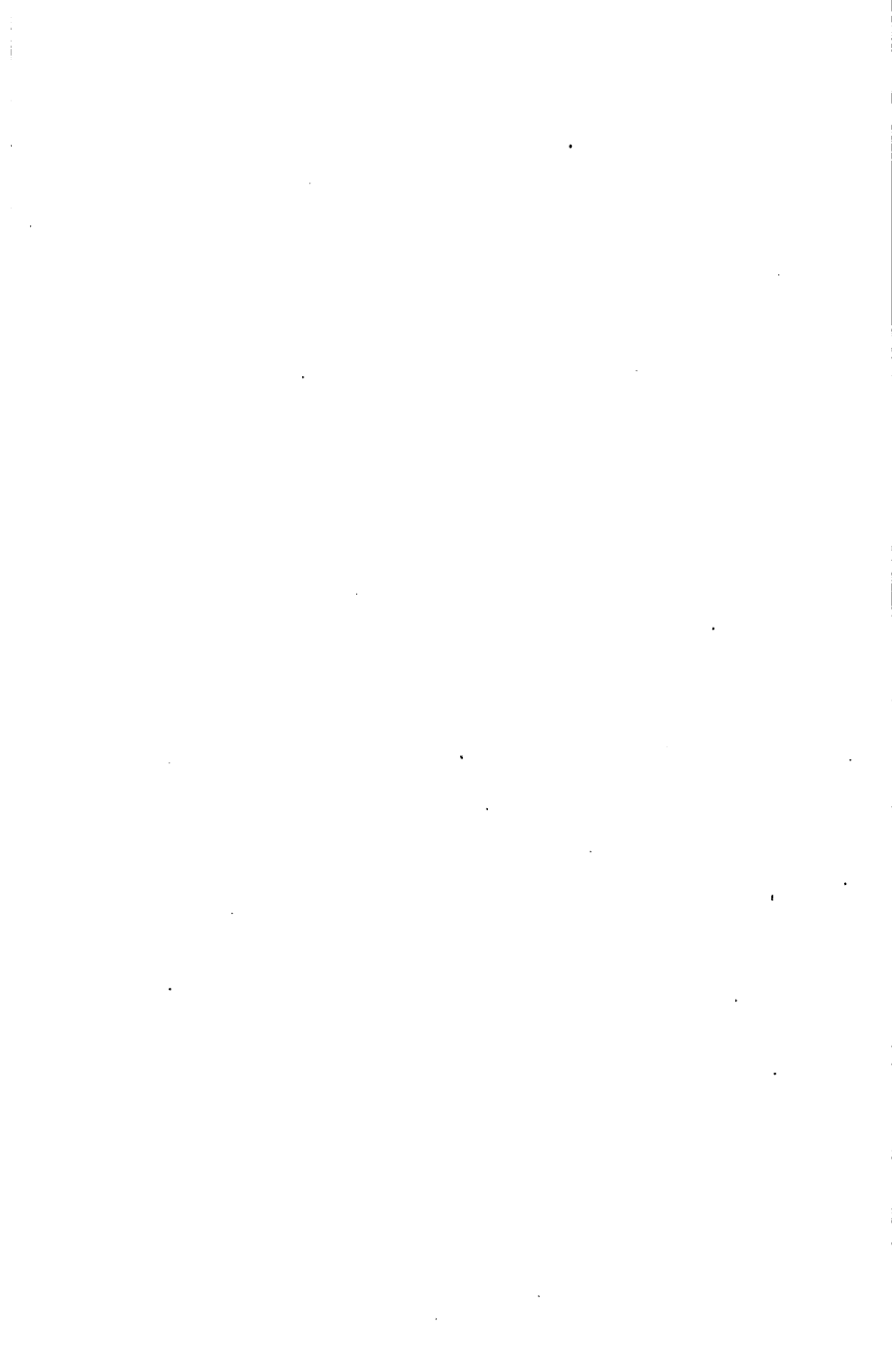
J. K.

ABERDEEN, April 1914.



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The Fixation of Atmospheric Nitrogen

INTRODUCTION.

UNTIL a few years ago, practically the only sources of inorganic nitrogen compounds were the sodium nitrate deposits of Chili, and the ammonium compounds obtained in the destructive distillation of coal. These sources supplied the raw material for the manufacture of the enormous quantities of nitric acid and ammonia used in the chemical industries. In addition, both sodium nitrate and ammonium sulphate are used as manures to supply the nitrogen necessary for plant growth. The great majority of plants are unable to assimilate nitrogen in the free form in which it occurs in the atmosphere, but take it up from the soil in the form of nitrates. During the slow decay of organic nitrogenous manures, the nitrogen is first converted into ammonium compounds, which are then transformed into nitrates by the nitrifying bacteria in the soil. The nitrogen in ammonium sulphate undergoes a similar transformation before its absorp-

tion by plants. Short accounts of the circulation of nitrogen in nature and its absorption by plants are given by v. Braun,¹ Stewart,² and Crossley.³ Owing to the intensive cultivation of food crops necessitated by the steadily increasing population of the world and the growing demand for a higher standard of living in all civilised countries, the natural supply of nitrates to the soil has to be augmented by the application of artificial nitrogenous manures, chiefly sodium nitrate and ammonium sulphate, and the consumption of these substances for manurial purposes has increased enormously since their introduction, and is steadily increasing. An excellent account of the Chili saltpetre industry, with relative statistics, is given by Norton.⁴ The export of nitrate from Chili rose rapidly from 935 tons in 1830 to 2,478,000 tons in 1912. The Chilian deposits contain enormous, but not unlimited, quantities of nitrate, and if the consumption increases in the future as it has done in the past they will be exhausted in a comparatively short time. Estimates of their probable life vary from twenty to fifty years.⁵

The total production of ammonia and ammonium compounds, the chief source of which is the nitrogen in coal, is not nearly so large as that of sodium nitrate, and, in the event of the exhaustion of the Chilian deposits, would not be sufficient to cover the demands of the chemical industries and of agriculture. The quantity of ammonia produced in Great Britain in 1912, calculated as ammonium sulphate, was 379,000 tons, and the world's total

production amounts at present to about 1,100,000 tons (1910).

In the atmosphere, which consists approximately of 21 per cent. oxygen and 79 per cent. nitrogen by volume, there is an inexhaustible store of nitrogen. It has been calculated that the atmosphere contains about 4,000,000,000,000,000 tons of nitrogen, or that in the air over every square mile of the earth's surface there are about 20,000,000 tons. In recent years an enormous amount of work has been done on the conversion of atmospheric nitrogen into technically important nitrogen compounds, especially into nitrates and ammonium compounds, since these are the forms of combined nitrogen for which both the chemical industries and agriculture make the largest demand.

In what follows we shall consider the more important attempts which have been made to utilise atmospheric nitrogen, and we may classify the methods employed under three main headings:—

(1) Conversion of nitrogen into nitric or nitrous acids and their salts.

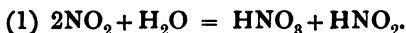
(2) Synthesis of ammonia and ammonium compounds from atmospheric nitrogen.

(3) Conversion of atmospheric nitrogen into compounds which readily yield ammonia.

SECTION I.

FIXATION OF ATMOSPHERIC NITROGEN AS NITRIC AND NITROUS ACIDS OR AS THEIR SALTS.

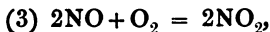
Summary of Process.—The first step in the fixation of atmospheric nitrogen as nitric or nitrous acids or their salts consists in oxidising the nitrogen to nitric oxide. The air itself contains the necessary oxygen, so that in the atmosphere we have an unlimited supply of the requisite raw materials. The NO is then further oxidised by excess of atmospheric oxygen to NO₂, and the NO₂ may be converted into nitrate or nitrite by choosing the proper conditions of absorption. When the NO₂ is absorbed by water, a mixture of nitric and nitrous acids is first produced.



Free nitrous acid is, however, unstable under ordinary conditions and decomposes as follows:—

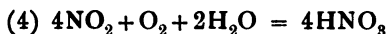


In presence of excess of oxygen the liberated NO is oxidised to NO₂,



which, in contact with water, goes through the same

series of reactions, until practically the whole of the original NO_2 is converted into nitric acid. By multiplying equation (1) by 3 and adding the result to equations (2) and (3) we obtain

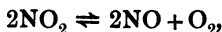


as the total equation representing the oxidation of NO_2 to nitric acid. The reaction represented by equation (4) is complete, however, only when excess of water is used, so that it is not possible to prepare concentrated nitric acid by this means.

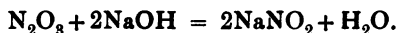
The absorption of NO_2 by alkalis under ordinary conditions of temperature and pressure takes place essentially according to the equation—



and results in the formation of equivalent quantities of nitrate and nitrite. Nitrogen peroxide, however, begins to dissociate above 140°C . according to the equation—



and the degree of dissociation increases with increasing temperature, until at about 620°C . the dissociation is complete. Now a mixture of equimolecular proportions of NO and NO_2 behaves towards alkali as nitrous anhydride, N_2O_3 , and on absorption produces practically pure nitrite,



The gas obtained by the oxidation of atmospheric nitrogen therefore consists, between 140° and 620° ,

of a mixture of NO , NO_2 , and air, the proportions depending on the temperature. By choosing the proper temperature it is, therefore, possible to obtain practically pure nitrite by absorbing the gas-mixture with alkali.

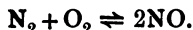
The thermal equilibrium between nitrogen, oxygen, and nitric oxide.—That nitric oxide or its oxidation products, nitrous and nitric acids, could be obtained by the direct union of nitrogen and oxygen at high temperatures has long been known. Thus by sparking a mixture of nitrogen and oxygen in presence of water or caustic potash, Cavendish obtained nitric acid or potassium nitrate. By the combustion of hydrogen and various other substances in a mixture of nitrogen and oxygen, nitrites and nitrates are also produced. A very complete bibliography of the older literature on the subject is given in Gmelin-Kraut.⁶

On the other hand, the decomposition of nitric oxide into nitrogen and nitrogen dioxide by electric sparks had been observed by Priestley, and numerous investigators⁷ subsequently studied its decomposition by heat or by the electric spark or arc. The results of these investigations, especially as regards the temperature at which decomposition becomes appreciable and the extent of the decomposition at different temperatures, are very conflicting.

It was gradually recognised that the primary product of the interaction of nitrogen and oxygen at high temperatures was nitric oxide, and that in the decomposition of nitric oxide by heat the primary products are nitrogen and oxygen. The occurrence

of higher oxides of nitrogen, such as NO_2 , or, in presence of water, of HNO_2 and HNO_3 , amongst the products of these reactions is due to the oxidation of the NO produced in the synthesis, or of the undecomposed NO in the decomposition, by the oxygen present. Further, it became evident from these numerous investigations that the extent to which NO may be synthesised from its elements or decomposed into its elements depended mainly on the temperature at which the reaction was made to take place, and that the action of the electric spark or arc, the combustion of hydrogen, etc., in bringing about the synthesis or decomposition was due to the high temperature produced by these means.

In the synthesis of nitric oxide from nitrogen and oxygen we are dealing with a typical reversible reaction,



At any given temperature the reaction leads to an equilibrium. According to the law of mass-action, the following relation must exist between the concentrations of N_2 , O_2 , and NO at equilibrium:—

$$K = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]},$$

where K is the equilibrium-constant, and the square brackets denote the concentrations of the enclosed substances. The value of K depends on the temperature, being constant for a given temperature and independent of the composition of

the original N_2-O_2 mixture. The same value of K should, of course, be obtained for a given temperature, whether we start with a mixture of N_2 and O_2 , with pure NO, or with a mixture of N_2 , O_2 , and NO. The concentration of NO at equilibrium for a given temperature is, however, dependent on the composition of the N_2-O_2 mixture with which we start, and it can be shown that the maximum concentration is obtained by starting with a mixture of N_2 and O_2 in equimolecular proportions. This is readily seen from the equilibrium equation. Since K is constant, the value of the numerator is a maximum when the product $[N_2] [O_2]$ is a maximum, and, for a given total pressure, this is the case when $[N_2] = [O_2]$.

The effect of temperature on the equilibrium can be inferred from the heat of the reaction—



At ordinary temperature the formation of 2 gram-molecules of NO is accompanied by the absorption of 43,200 calories.⁸ The reaction from left to right is, therefore, endothermic, and, according to van't Hoff's principle of mobile equilibrium, the equilibrium will be displaced by rise of temperature in favour of the formation of NO, the system formed with absorption of heat. With increasing temperature, therefore, the value of the equilibrium-constant K increases, and the concentration of NO present at equilibrium starting with a given N_2-O_2 mixture, is the greater the higher the temperature.

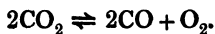
The relation between the equilibrium-constant K and the temperature is given by the equation—

$$\frac{d \log_e K}{dT} = \frac{-Q}{RT^2}.$$

Here Q is the heat of the reaction (in this case the heat of formation of 2 gram-mols. NO from 1 gram-mol. N_2 and 1 gram-mol. O_2 , namely $-43,200$ cal.), T is the absolute temperature, and R the gas-constant, the numerical value of which is 1.985 when the gram-calorie is the unit of energy. On integrating between the absolute temperatures T and T_1 , for which the respective equilibrium-constants are K and K_1 , we obtain, on the assumption that Q is independent of the temperature, and on changing from natural to common logarithms,

$$\log_{10} \frac{K}{K_1} = \frac{Q}{2.3R} \left(\frac{T_1 - T}{TT_1} \right).$$

The first attempt to determine accurately this equilibrium was made by Muthmann and Hofer.⁹ As the source of high temperature they used a high-tension alternating current arc. This was allowed to burn between platinum electrodes in a globe containing air long enough to ensure that equilibrium had been reached throughout the mass. The gases were then withdrawn and analysed. The temperature was determined by investigating under exactly similar conditions the dissociation of carbon dioxide into carbon monoxide and oxygen according to the equation—



From the observed degree of dissociation the temperature was obtained from the table given by Le Chatelier,¹⁰ who determined the degree of dissociation of carbon dioxide over a considerable range of temperature. Muthmann and Hofer, however, regard the temperature so determined as a minimum only, and admit that it may be considerably below the real temperature. The equilibrium was also approached from the other side by exposing NO to the action of the arc for at least half an hour, and then withdrawing and analysing the gas mixture. The equilibrium-constant determined by this method agreed fairly well with that obtained by the synthetic method. Thus at 1800° the equilibrium-constants obtained were: from air, $K = 8.97 \times 10^{-8}$; from nitric oxide, $K = 7.90 \times 10^{-8}$. The following table gives the mean value of the equilibrium-constant for different temperatures:—

Temp. C.	1825	1800	1590
K	0.0111	0.00841	0.000701.

The concentration of nitric oxide at equilibrium and the equilibrium-constant increase with increasing temperature, which agrees with the result predicted by theoretical considerations. Muthmann and Hofer regarded the equilibrium in the arc as purely thermal.

Nernst gives reasons for believing that the temperature of the arc used by Muthmann and Hofer was much higher than the 1800° C. which they assume, and on account of the uncertainty of the temperature determinations a new and more accurate

investigation of the NO equilibrium was undertaken by Nernst¹¹ and his co-workers Finckh¹² and Jellinek.¹³ A summary of the results obtained is given by Nernst.¹⁴

In the determination of such equilibria between gases at high temperatures, the gases leaving the reaction-chamber must be cooled to ordinary temperature before they can be analysed. If the cooling takes place slowly the equilibrium corresponding to the high temperature under investigation will be disturbed, and a new equilibrium reached for each temperature which the cooling gases assume, until a temperature is reached at which the velocity of the reaction is negligible. Below this temperature the composition of the gas mixture will undergo no further change, although the composition does not correspond to equilibrium at this temperature. If, however, the gases issuing from the reaction-chamber, in which equilibrium corresponding to the high temperature has been reached, are cooled rapidly enough to a temperature at which the reaction-velocity is negligible, it may be possible, by properly adjusting the rate of flow of the gases through the apparatus, to preserve at ordinary temperature the composition of the gases corresponding to equilibrium at the high temperature.

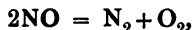
In the method employed by Nernst, dry atmospheric air was passed through a pipette-shaped platinum or iridium vessel contained in an electrically heated furnace which was maintained at a definite temperature. The gases left the reaction-chamber by means of a capillary outflow, in which the velocity

of flow of the gases was, therefore, increased compared with that in the reaction-chamber, thus hastening the passage of the gases through the danger-zone, in which a disturbance of the equilibrium might have occurred. The cooled gas leaving the capillary was then analysed, and the proportions of NO, N₂, and O₂ at equilibrium thus obtained. The equilibrium-constant for the particular temperature used could then be calculated. A full discussion of the problem of the preservation of the high temperature equilibrium and of the various criteria of equilibrium is given by Nernst¹¹ and by Haber.¹⁵

The equilibrium-constant $K = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$ can also be determined from measurements of the velocity of decomposition of NO into N₂ and O₂, and of the velocity of formation of NO from N₂ and O₂. If in the decomposition of NO x is the concentration of NO present at time t , then the law of mass-action gives for the rate of decomposition of NO

$$-\frac{dx}{dt} = k_1[\text{NO}]^2 - k_2[\text{N}_2][\text{O}_2],$$

where k_1 is the velocity-constant of the reaction



and k_2 the velocity-constant of the reverse reaction.

At equilibrium $-\frac{dx}{dt} = 0$, and, therefore,

$$K = \frac{k_1}{k_2} = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}.$$

By determining the velocity-constants k_1 and k_2 for a given temperature, the equilibrium-constant K for

that temperature may be calculated. Such velocity determinations have been carried out by Nernst and Jellinek, and the possible concentration of NO from air at various temperatures calculated from them.

Finally, the equilibrium conditions for still higher temperatures have been calculated by Nernst¹⁶ from experiments by Finckh, who measured the amount of NO produced by exploding mixtures of electrolytic gas ($2\text{H}_2 + \text{O}_2$) and air. The following table gives the results obtained by these various methods:—

<i>T</i> abs.	<i>x</i> (obs.).	<i>x</i> (calc.).	Observer.
1811	0.37	0.35	Nernst
1877	0.42	0.43	Jellinek
2023	0.52-0.80	0.64	„
2033	0.64	0.67	Nernst
2195	0.97	0.98	„
2580	2.05	2.02	Nernst-Finckh
2675	2.23	2.35	„

The second column gives the observed equilibrium concentration of NO from air at the abs. temperature *T*. In the third column are given the calculated equilibrium yields of NO. These have been obtained from the equation—

$$\log_{10} \frac{K}{K_1} = \frac{Q}{2.3R} \left(\frac{T_1 - T}{TT_1} \right)$$

by taking the concentration of NO from air at 2200° abs. as 0.99 per cent. If *x* is the percentage of NO at equilibrium, starting with air (79.2 per cent. nitrogen and 20.8 per cent. oxygen), then

$$K = \frac{x^2}{\left(79.2 - \frac{x}{2}\right) \left(20.8 - \frac{x}{2}\right)}.$$

From this equation K can be calculated if α is known, and α if K is known. The close agreement between the observed and calculated values of α is a strong argument in favour of the process, as carried out by Nernst, being a purely thermal one.

From the velocity measurements of Jellinek the following table has been constructed:—

T abs.	k_1 .	k_2 .	t .
1000	4.0×10	1.74×10^{-7}	81.62 years
1500	3.78×10^4	2.33×10^{-1}	1.26 days
1900	9.06×10^6	1.20×10^3	2.08 mins.
2100	1.40×10^8	5.55×10^4	5.06 secs.
2500	3.37×10^{10}	6.98×10^7	1.06×10^{-2} sec.
2900	8.07×10^{12}	5.48×10^{10}	3.45×10^{-5} ,,

k_1 and k_2 are the velocity-constants for the decomposition and formation of NO respectively at the absolute temperature T . t is the time required at T° abs. for the formation of half the possible concentration of NO from air. On the other hand, the times required for the decomposition of half a given quantity of pure NO at atmospheric pressure are 7.35×10^3 mins. at 900° abs., 5.80×10^2 mins. at 1100° abs., and 4.43×10 mins. at 1300° abs. From these figures it is evident that the equilibrium between N_2 , O_2 , and NO at very high temperatures is reached in an exceedingly short time, whilst at temperatures below about 1000° C. the rate of decomposition of NO is so slow as to be negligible in practice.

The theoretical considerations discussed above, which, as we have seen, are confirmed by the

experimental work of Nernst and his co-workers, indicated the conditions which must be observed in the technical production of nitric acid by the oxidation of atmospheric nitrogen. To obtain a high concentration of NO the air must be heated to as high a temperature as possible, and then cooled as rapidly as possible to a temperature at which the decomposition of NO takes place so slowly as to be practically negligible.

The Formation of Nitric Oxide under the Influence of the Electric Discharge.—For the attainment of the very high temperatures indicated by Nernst's work as necessary for producing high concentrations of NO, the most convenient means is the use of the electric arc, and this is the only method of bringing about the combination of nitrogen and oxygen which has met with technical success. The thermal explanation of the production of NO in the arc was for long universally accepted. The arc was regarded purely as a region of very high temperature, in which the thermal equilibrium was established practically instantaneously. The preservation of the high concentration of NO depended on the rapid removal of the equilibrium gases from the heated area and quick and efficient cooling. The more rapid the cooling the less was the decomposition of the NO formed at the high temperature. Occasional observations, such as those of v. Lepel,¹⁷ indicating that electrical influences played a part in the production of NO in the electrical discharge, were ignored. The purely thermal explanation, first put forward by Muthmann and Hofer and supported

by the work of Nernst, received strong confirmation as the result of numerous subsequent investigations.

When a high-tension arc burns in air between horizontal electrodes a true flame is formed, the air-flame. This was observed by M'Dougall and Howles,¹⁸ Muthmann and Hofer, and others, and its structure more closely investigated by Brode.¹⁹ The flame consists of three zones: (1) a brightly luminous bluish band of light joining the electrodes, surmounted by (2), a broader bluish-green zone, and (3) a feebly luminous brownish zone above this. In zone (1) the current is carried, and this zone has the highest temperature, as it is the only part which derives its heat directly from the current. An idea of the temperature of this zone is got from the fact that concentrations of NO as high as 8 per cent. were obtained from air under special conditions with such a flame, and this corresponds, according to extrapolation from Nernst's figures, to a temperature of about 3700° C. According to Brode the high concentrations of NO correspond to thermal equilibrium in zone (1). In zone (3) NO at high concentration from the hotter parts of the flame undergoes partial decomposition. This is proved by the fact that higher concentrations of NO are got by cooling this zone, *e.g.*, by withdrawing the gases by a water-cooled capillary, and thus preventing decomposition as far as possible. Brode further showed that in zone (2) decomposition of ozone probably takes place. This view is supported by the following considerations. In nitrogen or hydrogen alone the discharge has the

EVIDENCE FOR THERMAL EQUILIBRIUM 17

form of a single blue band, corresponding to zone (1) of the air-flame. In pure oxygen there are two zones, apparently identical with (1) and (2) of the air-flame, and Brode succeeded in detecting ozone in the oxygen-flame. This proves that ozone is formed in the high-tension arc, and explains the flame formation in pure oxygen and the reaction in zone (2) of the air-flame.

Evidence that the Reaction is purely Thermal.

—The most convincing evidence in favour of the purely thermal equilibrium in the high-tension arc discharge was furnished, however, by the work of Le Blanc and Nüranen²⁰ and of Grau and Russ.²¹ Le Blanc and Nüranen, using a high-tension alternating current arc between horizontal electrodes of Nernst filaments, found that the expression—

$$\frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = K \text{ or } \frac{[\text{NO}]}{[\text{N}_2]^{\frac{1}{2}}[\text{O}_2]^{\frac{1}{2}}} = K_1$$

remained practically constant in spite of great differences in the composition of the initial $\text{N}_2\text{-O}_2$ mixture (3·2 per cent. to 87·1 per cent. O_2). They, therefore, conclude that the combination of nitrogen and oxygen to nitric oxide in the arc obeys the law of mass-action—a strong argument in favour of a purely thermal equilibrium. Grau and Russ, by using a vertical arc burning in water-cooled glass or silica tubes, were able to avoid the distortion of the arc to a flame which occurs when the arc is burned between horizontal electrodes, and to obtain steadily burning arcs up to 7 cms. long. Using such high-tension arcs, they investigated the

applicability of the law of mass-action to the formation of NO. The gases were withdrawn from the arc by a water-cooled platinum capillary, thus ensuring rapid cooling and preservation of the NO. At first they found that the value of the constant K increased with increasing oxygen content of the initial gas mixture, and concluded that with increasing oxygen content the temperature of the arc increased. In support of this assumption, they found that with an arc of given length and given current strength, the voltage, and, therefore, the watt-consumption, increased with increasing oxygen content of the initial mixture. In their subsequent work they, therefore, took equality of watt-consumption as a criterion of approximate equality of temperature in their arcs. By sucking off the gases from the arc with a cooled capillary, they found that with a high velocity of flow of the gases past the arc the concentration of the NO was small, as evidently an excess of air was used. With diminishing velocity of flow the concentration of NO increased. By extrapolation the concentration of NO for zero velocity was obtained, and this represents the equilibrium concentration of NO in the arc. This was found to be 5.5 per cent. NO from air and 6.6 per cent. NO from a mixture of equal volumes of N_2 and O_2 , independent of the length of the arc. The values of the equilibrium-constant K calculated from these figures agree to within about 4 per cent. Grau and Russ, therefore, conclude that the mass-action law holds. From the concentration of NO they calculated that the temperature of their

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arc was ca. 3500° abs. They further showed that the equilibrium in the high-tension arc is not influenced by change of pressure (761-847 mm.), in agreement with the requirements of the law of mass-action for a reaction in which the number of molecules does not change. The effect of slow cooling of the gases is well seen in an experiment in which a concentration of 4.5 per cent. NO was obtained by sucking the gases from the middle of the arc, whereas just outside the arc, a few millimetres from the flame, the concentration was only 2.65 per cent. NO, indicating a decomposition of 40 per cent. of the original NO.

Another method of deciding whether the effect of the arc was purely thermal, or if electrical influences played a part in the formation of NO, was adopted by Foerster,²² and by Lee and Beyer.²³ They argued that if electrical influences came into play, the yield of NO per unit of energy supplied to the arc should be different for a direct and an alternating current discharge. They found the yields to be practically identical, however, and concluded that the reaction in the arc was purely thermal.

Berthelot's statement,²⁴ that no nitrous gases are produced by the action of the silent electrical discharge on air, was also used in support of the thermal explanation. This statement was, however, contradicted by later work of Berthelot himself,²⁵ and especially by the work of Warburg and Leithäuser,²⁶ who showed definitely that NO was produced by the action of the silent discharge on air. In this case there is no doubt that the formation of NO is due

to electrical influences, since the experiments were carried out at ordinary temperature, at which the concentration of NO demanded by the thermal equilibrium is practically zero; and Warburg²⁷ expressed the opinion that the formation of NO in the arc was not a purely thermal process, but that electrical influences, *e.g.* electronic collisions, also played a part.

The "Electrical" Production of Nitric Oxide.—
The most important contribution to the discussion of the relative importance of electrical and thermal effects in the production of NO in the high-tension arc is the brilliant experimental work of Haber and his co-workers. Haber and Koenig²⁸ seek to prove that the primary action in the high-tension arc, as in the silent discharge, is an electrical one—that the kinetic energy of the gaseous ions, and especially of the electrons produced in the arc, moving under the influence of the potential gradient between the electrodes, is utilised directly in the formation of NO when these ions and electrons collide with neutral molecules or with one another. The higher the potential gradient in the arc, the greater will be the kinetic energy of the moving ions and electrons, and the more effective the electrical production of NO. A condition which Haber and Koenig term an electrical equilibrium between nitrogen, oxygen, and nitric oxide will ultimately be reached, in which equal numbers of molecules of NO are formed and decomposed in a given time by electronic impacts. The electrical equilibrium differs from the purely thermal equilibrium. The position of the latter is

determined only by the temperature and the law of mass-action, whilst in an electrical equilibrium there is in addition a definite expenditure of electrical energy per unit of time, the amount of which determines the magnitude of the deviation from the purely thermal equilibrium for the same temperature. Since an electrical equilibrium is accompanied by an expenditure of free energy compared with the thermal equilibrium for the same temperature, we may say in general that the electrical equilibrium for a given reaction will correspond to the thermal equilibrium at a higher temperature. Thus the concentration of O_3 in thermal equilibrium with O_2 , of CO and O_2 in thermal equilibrium with CO_2 , of N_2 and H_2 in thermal equilibrium with NH_3 , are infinitesimal at ordinary temperature. Under the influence of the silent discharge, however, concentrations of O_3 , of CO and O_2 , and of N_2 and H_2 corresponding to thermal equilibrium at much higher temperatures are obtained at ordinary temperature. Similar results were obtained by Warburg and Leithäuser for NO . They obtained measurable concentrations of NO by the action of the silent discharge on air at ordinary temperature, although the concentration of NO in thermal equilibrium with N_2 and O_2 at ordinary temperature is practically zero. That the concentration of NO corresponding to electrical equilibrium at ordinary temperature is preserved after the electrical influence is removed, is due merely to the extremely small velocity of decomposition of NO at ordinary temperature. If, on the other hand, the temperature is so high that the thermal equilibrium

is reached practically instantaneously, then the concentration of NO will correspond to the purely thermal equilibrium; for any excess of NO produced by the electrical equilibrium will immediately decompose owing to the rapidity with which the thermal equilibrium is reached. It therefore follows that the thermal phenomena can be subordinated to the electrical only in a temperature interval in which the decomposition velocity of NO is comparatively slow. Haber and Koenig realised these conditions by burning a high-tension, alternating current vertical arc under diminished pressure in a narrow water-cooled glass or quartz tube between electrodes of iron, platinum, or Nernst filaments. Under these circumstances the arc filled the narrow tube practically completely. Different mixtures of oxygen and nitrogen were passed *slowly* through the arc, the gas being made to enter and leave the tube some distance from the electrodes, so as to avoid the effects of the complex electrical conditions in the immediate neighbourhood of the electrodes. Under these conditions, concentrations of NO up to 9.8 per cent. were obtained from air, and up to 12.5 per cent. from a mixture of 4 vols. oxygen and 1 vol. nitrogen ("inverted air"). The pressures employed ranged from 25 to 140 mm., and it was found that the highest concentration of NO was got at a pressure of ca. 100 mm. With a mixture of equal volumes of nitrogen and oxygen a maximum concentration of 14.5 per cent. NO was obtained, and the same concentration was reached by passing pure NO through the arc under the same conditions. The main

arguments used by Haber and Koenig in support of the electrical theory of NO formation may be summed up as follows:—(1) A concentration of 9·8 per cent. NO corresponds, according to the thermodynamic calculation, to a temperature of ca. 4100° C., and 12·5 per cent. to ca. 4600° C. Haber and Koenig give reasons for believing that the temperature of their arc was certainly below 3000° C., and at most probably only a few hundred degrees above the melting point of platinum (1800° C.), a temperature at which the thermal equilibrium is comparatively immobile, so that NO formed by electronic collisions escapes thermal decomposition. (2) These high concentrations of NO were obtained when the gases were passed *slowly* through the arc, and no special precautions were taken to rapidly freeze the equilibrium. (3) According to the thermal explanation the results with air and “inverted air” should have been the same, whereas they differ very considerably. (4) That an electrical equilibrium was reached is proved by the identity of the results obtained, starting with pure NO and with a mixture of equal volumes of nitrogen and oxygen. Haber and Koenig, therefore, conclude that for the production of NO by the electrical discharge, the use of cold arcs will give the best results, and not, as hitherto held the attainment of very high temperatures and rapid freezing of the equilibrium. The technical use of such arcs, however, offers very considerable difficulties, and up to the present they have not been introduced on a technical scale.

Haber and Koenig also critically examined

previous work on the production of NO in the high-tension arc in the light of their own results. With high-tension arcs burning between electrodes which are not too close together, the results obtained agree well apparently with the thermal explanation, since concentrations of NO are obtained which indicate a probable temperature of ca. 3000° C. for the arc. This temperature is calculated from Nernst's values for much lower temperatures, but the extrapolation is probably justified. Also the decomposition velocity of NO for such temperatures, extrapolated from the data of Nernst-Jellinek, do not exclude the attainment of the NO-concentrations reached in such arcs. According to Haber and Koenig, the apparent agreement with the thermal theory in these cases is due to secondary thermal decomposition, on account of the high temperature, of the NO produced electrically in the arc.

The matter is much more doubtful in the case of short high-tension arcs. With such alternating current arcs Muthmann and Hofer obtained NO-concentrations up to 6·7 per cent., Brode up to 7·2 per cent., and M'Dougall and Howles up to 7·4 per cent. Concentrations of ca. 7 per cent. correspond to a calculated temperature of ca. 3500° C. for the arc, a temperature which might quite well be reached as a result of the discharge. On the other hand, the thermal equilibrium at such temperatures is so mobile that it would be practically impossible to preserve these NO-concentrations even by rapid cooling. Haber and Koenig believe that in such arcs the high temperatures, calculated thermo-

dynamically, were not reached. They also show that in such high-tension, alternating current arcs the temperature must vary with enormous rapidity at every part of the arc, so that it is practically meaningless to speak of a mean temperature in such a case and apply it to the calculation of the thermodynamic equilibrium.

The results of Haber and Koenig for high-tension, alternating current arcs have been confirmed by Morden,²⁹ Holwech,³⁰ and Holwech and Koenig³¹ for very short, direct current arcs with cooled anodes. The anode consisted of a water-cooled silver capillary, through which the gases were withdrawn. In some cases the cathode was specially heated, but this made no essential difference to the results. Concentrations of NO up to 9.5 per cent. were reached when the velocity of flow of the gases was made as small as possible. The most favourable pressure was 300-500 mm. The potential-gradient in the arc was carefully investigated, and it was found that, with a given length of arc, the stronger the field the greater was the maximum concentration of NO attainable, so long as the temperature of the arc was not too high. If the temperature was allowed to rise too much, thermal influences got the upper hand of electrical, and the maximum NO-concentration diminished. It was shown that the maximum temperature of the arc was probably about 3000° abs., which corresponds to a concentration of only ca. 4 per cent. NO for thermal equilibrium, whilst 9.5 per cent. NO would require a temperature of over 4000° abs., which was certainly not reached. Similar results were obtained

by Haber, Koenig, and Platou³² using a 7.5 cm. direct current arc burning in a narrow, vertical water-cooled tube.

From a study of the admirable work of Haber and his collaborators, it is impossible to avoid the conclusion that the production of NO in the high-tension arc is primarily electrical, and that the comparatively low concentrations of NO in technical arcs are due to subsequent thermal decomposition of the electrically produced NO, owing to the high temperature conditions prevailing in such arcs.

Briner and Durand³³ and Guye³⁴ express the opinion that the thermal explanation is sufficient to account for the formation of NO in the arc. Their view is that our knowledge of the NO-equilibrium at high temperatures is based only on a wide extrapolation from values determined for much lower temperatures, and is, therefore, subject to all the uncertainties of such an extrapolation. Further, at high temperatures subsidiary reactions, such as dissociation of N_2 and O_2 to ions or atoms, probably take place. By the union of these ions or atoms greater concentrations of NO may be reached than are predicted by the extrapolation. Haber and Koenig quite admit this possibility, and, indeed, discuss it in their earlier papers. They maintain, however, that their results cannot be explained by the purely thermal theory, which demands for the highest concentrations of NO the highest arc temperature and the most rapid cooling. It is scarcely possible that in the cooled arcs traversed by a slow stream of gas

which they employed, the temperature was higher and the cooling more rapid than in the uncooled arcs provided with special devices for rapidly freezing the equilibrium, used by previous investigators, who in every case obtained much lower NO-concentrations.

Activation of Nitrogen and Oxygen prior to Formation of Nitric Oxide.—In a recent investigation Fischer and Hene³⁵ seek to prove that in the high-tension arc the oxidation of the nitrogen to NO is preceded by an activation of the oxygen, but not of the nitrogen. They suggest a chemical explanation for the high concentrations of NO obtained by Haber and Koenig in the cooled arc, and for the apparent deviations from the law of mass-action found by Grau and Russ²¹ in presence of high concentrations of oxygen. They suggest that in both cases the conditions are favourable to ozone formation, and that it is the oxidation of the nitrogen by ozone which gives the high NO-concentrations. They were at first inclined to the view that an activation of the nitrogen, *e.g.* by dissociation into atoms at the high temperature, preceded the formation of NO. This suggestion was first put forward by Escales,³⁶ and was rendered probable by the discovery of an active form of nitrogen by Strutt,³⁷ who obtained it by the action of a jar-discharge with spark-gap on nitrogen under very low pressure. Strutt inclines to the view that his active nitrogen consists of nitrogen atoms. He finds, however, that it gives no NO with oxygen. Fischer and Hene, therefore, conclude that no

activation of nitrogen in the arc takes place, and they regard this conclusion as confirmed by their experimental work. The results on which they base their view that the formation of NO in the arc is due to an activation of the oxygen and not of the nitrogen are as follows: (1) With spark-discharge.—If the pure gas given in Column I. of the accompanying table is subjected to the spark-discharge whilst issuing from a quartz capillary, and the sparked gas leaving the capillary is immediately allowed to mix with the unsparked gas given in Column II., the relative concentrations of NO given in Column III. are obtained, the concentration from sparked N_2 and unsparked O_2 being taken as unity.

Sparked gas.	Unsparked gas.	Parts NO.
N_2	O_2	1.0
"	Air	1.5
Air	N_2	2.0
"	Air	3.5
"	O_2	4.0
O_2	Air	5.0
"	N_2	6.5

The concentration of NO from sparked O_2 and unsparked N_2 , for example, is 6.5 times that from sparked N_2 and unsparked O_2 . (2) With high-tension arc.—Air was passed through a high-tension arc burning between horizontal iron electrodes, and the air leaving the arc was immediately mixed with a current of ordinary oxygen, air, or nitrogen. Different concentrations of NO were obtained according to the gas used for mixing with the

ACTIVATION OF NITROGEN AND OXYGEN 29

arced air. The concentrations of NO given in the following table are calculated on the volume of air sent through the arc :—

Arced gas.	Unarced gas.	Per cent. NO by vol.
Air	N ₂	5·9
„	Air	7·4
„	O ₂	7·8

More NO is obtained, therefore, when air from the arc streams into oxygen and is cooled than when it streams into air or nitrogen. The different concentrations of NO might be explained by diffusion of the mixing gas into the arc flame. In that case the watt-consumption of the arc should have changed (Grau and Russ), which it did not. The increasing NO-concentration with increasing oxygen-content of the mixing gas must, therefore, be due to activation of the oxygen. (3) With silent discharge.—Ehrlich and Russ³⁸ found that both NO and O₃ were formed by the prolonged action of the silent discharge on air at ordinary temperature. It is not known certainly, however, whether O₃ oxidises nitrogen at ordinary temperature, as the reaction velocity is so slow. If the oxidation of nitrogen is attributed to the primary formation of O₃, then the concentration of NO produced by the action of the silent discharge on air must be greater the higher the temperature, owing to the greater velocity of the reaction between ozone and nitrogen. Fischer and Hene passed air through an ozoniser which could be heated to a definite temperature, and obtained

the following concentrations of NO at different temperatures:—

Temp. C.	20°	380°	430°	510°	700°.
Per cent. NO	0.00	0.02	0.02	0.04	0.06.

No NO was formed at 700° without the discharge, and no O₃ was observed except at 20°, yet the concentration of NO increases with increasing temperature. From the results of these experiments Fischer and Hene conclude that the formation of NO in the high-tension arc is preceded by an activation of the oxygen. The energy supplied to the arc causes dissociation of the oxygen molecules to atoms. Outside the arc these atoms react with O₂-molecules to form ozone. Whether the oxygen atoms also act directly with nitrogen cannot at present be determined. They point out that the reaction $2\text{O}_3 + \text{N}_2 = 2\text{NO} + 2\text{O}_2$ is exothermic, liberating 250,000 cal. They suggest that better yields of NO might be obtained technically by passing pure oxygen through the arc instead of air, and then mixing it rapidly with nitrogen.

Koenig³⁹ criticises Fischer and Hene's conclusions that only the oxygen and not the nitrogen is activated in the arc. He points out that it is remarkable that, if no activation of nitrogen takes place, any NO at all should be obtained when sparked nitrogen mixes with unsparked oxygen. He considers that in no case was pure nitrogen or oxygen sparked, but that with the arrangement used by Fischer and Hene, owing to the rapid expansion and contraction of the gas in the capillary

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during the high-frequency discharge, the mixing gas was drawn into the capillary, so that a mixture of nitrogen and oxygen was always sparked. The same doubt is expressed with regard to the high-tension arc experiments, where rapid expansion and contraction must also cause mixing of the gases. He maintains that admixture of 5 per cent. of oxygen with the air, which could easily raise the NO-concentration from 7.4 to 7.8 per cent., would hardly be shown with certainty by the watt-meter. He further asks why the experiments with the arc were not carried out according to the same scheme as with the spark, and especially why the crucial experiment of passing oxygen only through the arc and subsequently mixing it with nitrogen was omitted. Koenig concludes that Fischer and Hene have failed to prove their case. He points out that the facts that Strutt's active nitrogen does not react with oxygen, and that ordinary nitrogen is not oxidised by ozone, favour the view that a simultaneous activation of both gases must take place in order that they may react. These conditions are fulfilled in the arrangement used by Haber and Koenig,²⁸ where both gases are ionised.

Fischer and Hene reply to Koenig in a more detailed account of their work.⁴⁰ They explain the formation of NO when sparked nitrogen passes into unsparked oxygen by the production of active oxygen, by the action of the glowing nitrogen on the oxygen. The same explanation accounts for the difference between the action of arced air on oxygen and on nitrogen. In the former case new active oxygen is

formed by the action of the heated gas issuing from the arc, whilst in the latter case this is impossible. In support of the non-activation of the nitrogen they also quote Brode's observations on the appearance of the high-tension arc in different gases (p. 16), and the recent work of Compton⁴¹ and Tiede,⁴² who independently arrived at the conclusion that the phenomena attributed by Strutt to active nitrogen are really due to admixture of traces of oxygen with his nitrogen. Strutt,⁴³ however, maintains that this is not the case, and that the phenomena are observed with nitrogen free from every trace of oxygen, and this is confirmed by Koenig and Elöd.⁴⁴ Fischer and Hene deny that any admixture of the gases takes place, and state that in the arc experiments no variation in the watt-consumption was shown by a sensitive watt-meter.

Although the results of Fischer and Hene are of great interest, it is difficult, from a study of their apparatus, to avoid the suspicion that mixing of the gases did take place to some extent.

An important contribution to the question of the mechanism of NO-formation by the electrical discharge is made by Lowry.⁴⁵ He describes experiments in which a current of air was submitted to the action of the silent discharge in an ozoniser, or to the action of the spark-discharge, or to a combination of the two. A very delicate spectroscopic method, depending on the photographing of the NO₂-spectrum in a column of gas 64 ft. long, was used to detect NO₂ in the air so treated. A concentration of NO₂ of $\frac{1}{8000}$ part by volume could

be detected with certainty. Under ordinary conditions no NO_2 was found when air was passed through the ozoniser alone or through three spark-gaps alone. When the air was passed first through the ozoniser and then through the spark-gaps, NO_2 was formed. This agreed with the observation of Cramp and Hoyle⁴⁶ that the yield of NO_2 from the arc discharge can be increased by ozonising the air supply. An almost equal concentration of NO_2 was obtained, however, by passing the air first through the spark-gaps and then through the ozoniser. This was surprising, as ready-made NO_2 is bleached by passing through the ozoniser, being probably oxidised to N_2O_5 or HNO_3 . It was next found that a spectrum of only slightly less intensity was got by passing air currents through the ozoniser and spark-gaps in parallel, and then mixing the two air currents. From a critical examination of these facts Lowry concludes that they can be explained only by assuming that the spark-discharge produces an oxidisable form of nitrogen ("atomised" or "ionised" nitrogen), which is readily oxidised by ozone, but not by oxygen. The most efficient way to oxidise it is to produce it in an atmosphere already charged with ozone; rather less efficient is to pass the air in which it is produced directly into the ozoniser; less efficient still is where the oxidisable nitrogen is mixed with ozonised air in a chamber a few feet away from the discharge apparatus. The slight but clearly marked gradation in the amount of NO_2 produced in these three cases is evidence of the instability of the oxidisable nitrogen, which appears

to revert in a few seconds to a form which is oxidisable neither by oxygen nor by ozone. These experiments seem to prove that an active variety of nitrogen can be produced by the electrical discharge in air at ordinary pressure. It differs from Strutt's active nitrogen, which gives no oxides of nitrogen with ozone. In view of his results, Lowry thinks it is not unreasonable to ask whether the production of oxides of nitrogen by the electrical discharge in all its forms is not due to the interaction of active nitrogen and active oxygen, either as ozone or atomic oxygen. His work strongly supports Haber and Koenig's view that both the oxygen and nitrogen are activated in the high-tension arc.

The Yield of Nitric Acid in the Arc.—By the yield of nitric acid is meant the quantity of acid produced per unit of electrical energy expended in its production, and is generally expressed in grams HNO_3 per kilowatt-hour or in kilograms HNO_3 per kilowatt-year. A high concentration of NO in the gases leaving the arc does not necessarily mean a high yield of HNO_3 . Thus when the velocity of passage of the air through the arc is large, much of the gas does not enter the arc or become strongly heated. The portion of the air which has been highly heated by contact with the arc, and which contains much NO , is, however, rapidly cooled by mixing with the excess of cold air, and the decomposition of the NO is thus prevented to a large extent. With a less rapid flow of air through the arc at the same temperature, the concentration of NO in the issuing gas may be greater on account of the smaller dilution with excess

of cold air, but, owing to less efficient cooling, a larger proportion of the NO formed at the highest temperature of the arc will be lost by decomposition, and the yield of HNO_3 may be less than with a high velocity of flow. Too great dilution with cold gas must, however, be avoided, since the more dilute the gas, the larger the proportion of oxides of nitrogen which escape absorption. Assuming that the reaction in the arc is a purely thermal process, several investigators have calculated the theoretical yield of HNO_3 . Thus Haber,⁴⁷ assuming the temperature of the arc to be 4200°C ., calculates as follows. From the thermodynamic extrapolation the composition of the equilibrium mixture at this temperature, starting with air, is 10 per cent. NO, 16 per cent. O_2 , 74 per cent. N_2 . Ten mols. of NO will yield by a series of spontaneous reactions 630 grams of HNO_3 . To get this amount of HNO_3 we must, therefore, heat 100 mols. of N_2 and O_2 to 4200°C . Assuming the specific heat per mol. of the permanent gases at the temperature $t^\circ\text{C}$. to be represented by the formula $6.8 + 0.0006t$, we find the amount of heat required to raise the 100 mols. to 4200°C . to be—

$$100(6.8 + 0.0006 \times 4200)4200 = 3,914,400 \text{ cal.}$$

To this must be added—

$$10 \times 21600 = 216,000 \text{ cal.,}$$

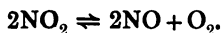
the heat of formation of 10 mols. of NO from N_2 and O_2 . The total heat expenditure is, therefore, 4,130,400 cal. = 4.71 kilowatt - hours for 630 grams HNO_3 . The yield is, therefore, 134 grams

HNO_3 per kilowatt-hour, or 1174 kilos. HNO_3 per kilowatt-year. A similar calculation for a temperature of 3200°C . gives 93.5 grams HNO_3 per kilowatt-hour, or 819 kilos. per kilowatt-year. Lowering the temperature thus diminishes the possible yield. On the other hand, there will be a smaller loss of NO owing to decomposition during cooling at the lower temperature, and the loss of heat by radiation will be much less at 3200° than at 4200°C .

It is of interest to compare the yields obtained by different investigators. Rayleigh,⁴⁸ who burned the arc in a mixture containing 36 per cent. N_2 and 64 per cent. O_2 , obtained ca. 50 grams HNO_3 per K.W.H. M'Dougall and Howles,¹⁸ who were the first to thoroughly investigate the production of HNO_3 from air, obtained 34 grams HNO_3 per K.W.H. from air, and 67 grams from the mixture used by Rayleigh. The doubling of the yield they attribute to mass-action, but, according to Haber,⁴⁹ this explanation is insufficient. They also found that the yield increased with the watt-consumption (increased current-strength) only up to a certain point, beyond which it remained practically stationary, the excess of electrical energy being lost by radiation and conduction. This result was confirmed by Scheuer⁵⁰ and by Grau and Russ, who obtained, with their vertical arcs, 52 grams HNO_3 per K.W.H. with a 3 cm. arc, and 62 grams with a 5 cm. arc, and concluded that longer arcs would give even higher yields. They also showed that a higher yield was obtained from a mixture of equal volumes of nitrogen and oxygen than from air, as required by

the law of mass-action. The yields obtained with the alternating-current cooled arcs used by Haber and Koenig were investigated by Haber, Koenig, and Platou. A yield of 57 grams per K.W.H. was reached, the concentration of NO being 3·4 per cent. Much higher yields were obtained with the cooled direct current arc. Thus Morden obtained up to 90 grams per K.W.H., Holwech, and Holwech and Koenig up to 80 grams per K.W.H. Although these yields do not differ greatly from those in technical arcs (60-75 grams per K.W.H.), they are obtained with much more favourable NO-concentrations. Thus Holwech obtained 60-70 grams per K.W.H. with ca. 4 per cent. NO, whilst the NO-concentration reached in technical work is only ca. 2 per cent. This Holwech attributes to the much steeper potential gradient used in his arc, and consequent increased ionisation.

Oxidation of Nitric Oxide.—Richardson⁵¹ showed that NO₂ begins to dissociate into nitric oxide and oxygen above ca. 140° C. The degree of dissociation increases with increasing temperature, and at ca. 620° C., under ordinary pressure, the dissociation is complete according to the equation—



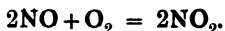
The following table shows the degree of dissociation at various temperatures and ordinary pressure—

<i>t</i> ° C.	184°	279°	494°	620°.
Per cent. NO ₂ dissociated	5·0	13·0	56·5	100·0.

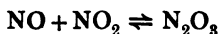
The oxidation of NO formed at the high temperature

of the arc does not begin, therefore, until the temperature has fallen below 620° , and cannot be complete above ca. 140° .

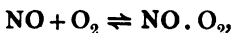
According to Raschig⁵² the oxidation takes place in two stages. The first reaction corresponds to the formation of N_2O_3 and takes place rapidly, whilst in the second stage the N_2O_3 is more slowly oxidised to NO_2 . Lunge and Berl,⁵³ on the other hand, found that the oxidation took place with measurable velocity as a trimolecular reaction according to the equation—



Nitrogen trioxide cannot be formed in any considerable concentration during the oxidation, since, under ordinary conditions, it is practically completely dissociated into NO and NO_2 .⁵⁴ The work of Schmidt and Böcker⁵⁵ and of Le Blanc⁵⁶ indicates, however, that in a mixture of NO and NO_2 —and such a mixture is formed during the oxidation of NO by air—the equilibrium



exists. The concentration of N_2O_3 at equilibrium is, however, very small. Foerster and Blich⁵⁷ found that the velocity of oxidation of NO by oxygen has a small negative temperature coefficient between 0° and 100° . They explain this by assuming that a "primary" oxide is first formed, *e.g.*—

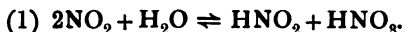


which then reacts with a second molecule of NO to give NO_2 —

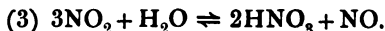


The first reaction is reversible, and tends to an equilibrium, which, with increasing temperature, favours the dissociation of the "primary" oxide. The smaller concentration of the latter at the higher temperature more than counteracts the greater velocity of the reaction between "primary" oxide and NO. Holwech⁵⁸ also found that the oxidation of NO to NO₂ was a comparatively slow reaction.

Absorption of Oxides of Nitrogen by Water.—A thorough investigation of the action of NO₂ on water was made by Foerster and Koch.⁵⁹ (A discussion of previous work is also given in their paper.) The formation of HNO₃ by the action of NO₂ on water is represented by the following reversible reactions:—



The total reaction is—



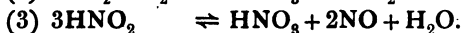
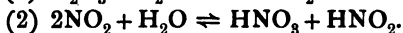
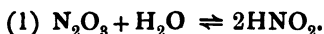
According to the law of mass-action, therefore, definite partial pressures of NO₂ and of NO correspond to a given concentration of HNO₃. The NO and NO₂ pressures are, however, influenced by the equilibrium $\text{NO} + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_3$, and by the solubility of N₂O₃ in concentrated HNO₃, especially at low temperatures. Further, in presence of excess of oxygen equilibrium (2) and, therefore, also equilibrium (1) is continuously disturbed by the reaction $2\text{NO} + \text{O}_2 = 2\text{NO}_2$, so that a given quantity of NO₂ must ultimately be completely converted into HNO₃. Foerster and Koch show that when a mixture of

nitrogen peroxide and oxygen, prepared from 1 vol. NO and 2 vols. O_2 , is led into water, the formation of HNO_3 takes place very rapidly until the concentration of HNO_3 is ca. 40 per cent. The absorption of nitrogen peroxide then becomes gradually slower until 50 per cent. HNO_3 is reached, beyond which concentration the rate of absorption rapidly diminishes. At ordinary temperature it is not possible to obtain a stronger acid than 68-69 per cent. by the action of nitrogen peroxide and oxygen on water. This limiting concentration of HNO_3 is explained by the diminution of the active mass of free water with increasing concentration of HNO_3 , owing to hydrate formation with HNO_3 , which diminishes the velocity of reaction (3), and to the increasing concentration of HNO_3 vapour in the gaseous phase with increasing concentration of the aqueous acid. The stronger the acid, the more HNO_3 does the gas current remove in the vapour it carries along with it. The concentration of HNO_3 reached is due to an equilibrium between these various factors. The lower the concentration of NO_2 in the gas mixture, the lower will be the limiting concentration of HNO_3 attainable, since the velocity of the reaction between NO_2 and water diminishes with diminishing NO_2 concentration, whilst the presence of a large excess of foreign gases accelerates the evaporation of HNO_3 from the solution. The following limiting concentrations of HNO_3 were obtained at ordinary temperature from air containing various amounts of NO_2 :—

Per cent. NO_2 in air	1	2	5
conc. HNO_3	ca. 46	ca. 52	>55 per cent.

Since the concentration of NO_2 in the gases produced technically by the combustion of nitrogen in the arc contain 1-2 per cent. NO_2 , it should be possible to obtain 46-52 per cent. HNO_3 by absorption with water.

Briner and Durand⁶⁰ studied the effect of temperature and pressure on the equilibrium between nitric and nitrous acids and oxides of nitrogen. They conclude that this equilibrium comprises three reversible reactions—



The action of NO on HNO_3 tends to produce nitrous anhydride; the greater the pressure of NO , and the greater the concentration of HNO_3 , the more readily does this take place. The effect of increase of temperature is to lower the ratio $\text{HNO}_2:\text{HNO}_3$, since reaction (3) is endothermic. High pressure and low temperature, therefore, favour the formation of HNO_2 , and the reverse conditions the formation of HNO_3 . The equilibrium corresponding to equation (3) has also been investigated by Ssaposchnikoff,⁶¹ and more recently by Lewis and Edgar.⁶²

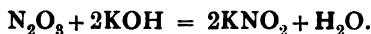
Absorption of Oxides of Nitrogen by Alkalies.—

When nitrogen peroxide is absorbed by alkalies, a mixture of nitrate and nitrite in practically equimolecular proportions is obtained—

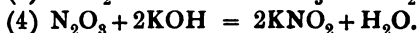
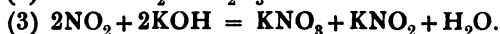
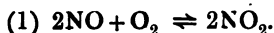


A mixture of NO and NO_2 in equimolecular proportions behaves as N_2O_3 , and gives on absorption by

alkalies practically pure nitrite, together with a little nitrate and NO .⁶³



When a mixture of nitric oxide and air or oxygen is absorbed by alkali, nitrite predominates, and the sooner the absorption takes place after admixture the greater is the proportion of nitrite found. Thus when air containing nitric oxide from the arc flame is passed through potassium hydroxide solution, nitrite is always in excess of nitrate, and the excess is greater when the gases are sucked directly out of the flame and absorbed at once. Le Blanc⁵⁶ explains this behaviour by assuming that during the absorption of a mixture of nitric oxide and air by alkali, in which the NO is undergoing oxidation to NO_2 , the following reactions take place:—



Reactions (2) and (4) take place rapidly, and although the concentration of N_2O_3 in the gas is always small (p. 38), the equilibrium is continually disturbed by the absorption of the N_2O_3 . Fresh quantities are formed from NO and NO_2 , and this goes on until either the NO or the NO_2 is exhausted. Reaction (3) is comparatively slow.⁶⁴ Foerster and Blich⁵⁷ confirmed Le Blanc's assumption that in a gas in which only part of the NO is oxidised to NO_2 , the equilibrium $\text{NO} + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_3$ exists, and that alkali absorbs principally N_2O_3 from such a mixture, so

that it behaves to alkali as if it consisted of N_2O_3 . They showed that liquid N_2O_3 is absorbed much more rapidly by alkali than N_2O_4 . A mixture of NO and NO_2 is, therefore, much more rapidly and completely absorbed by alkali than pure NO_2 .

These considerations explain the technical production of almost pure nitrite when the hot gases from the arc are absorbed by alkali. Such hot gases contain a mixture of NO and NO_2 , since above 140° the oxidation of NO cannot be complete (p. 37). In a mixture of NO and air, in which the concentration of NO is very small, the velocity of oxidation of NO to NO_2 will be very slow, in accordance with the law of mass-action. Such a mixture leaves the last of the acid absorption towers in the technical production of HNO_3 from air. At the rate at which the gas current is passed through the absorption apparatus, there is insufficient time for the complete oxidation of the NO before the gas current reaches the alkali absorption towers, so that in them mainly nitrite is formed.

By the action of ozone on nitrogen peroxide Helbig⁶⁶ found that N_2O_5 was rapidly formed, which can be absorbed by water giving concentrated HNO_3 . Foerster and Koch⁶⁹ also found that ozone oxidises NO_2 , even when very dilute, very rapidly to N_2O_5 . By leading a mixture of dilute NO_2 and ozone into water it is easy to get HNO_3 of more than 80 per cent. strength. Owing to the great velocity of the reaction between NO_2 and O_3 , the addition of ozonised air might be utilised technically for the conversion of the very dilute nitrous gases leaving the absorption

towers into HNO_3 . At present, however, ozone evidently cannot be produced sufficiently cheaply to make its use remunerative.

Technical Manufacture of Nitrates and Nitrites.

Of the innumerable processes and forms of apparatus which have been patented⁶⁶ for effecting the union of nitrogen and oxygen by means of the electrical discharge, only those which have met with technical success can be described here. Among the pioneers of the synthetic nitrate industry must be mentioned P. A. Guye and his co-workers C. P. Guye and Naville,⁶⁷ who, since their first patents in 1895, have made constant improvements in their apparatus, and have contributed materially to the solution of the problem of synthesising nitric acid from air. The work of Moscicki and Kowalski⁶⁸ must also be noticed. Great ingenuity has been displayed in the design of their furnaces, some of which, from tests on a small scale, give promise of technical success.

The earlier inventors aimed at rapidly heating the air to as high a temperature as possible and quickly cooling it. To avoid heat losses as much as possible they used a large number of low-current, high-tension arcs instead of a single heavy-current arc. By suitable arrangements a large number of long, slender arcs were made to form, expand through a large volume of air and break, so that rapid heating and cooling was ensured. The first attempt to work such an apparatus on a technical scale was made by

Bradley and Lovejoy⁶⁹ in 1902, at Niagara Falls, but failed owing to high initial cost, the small units which were employed, and the heavy repair charges caused by the complicated nature of the apparatus.

The processes at present in successful technical operation depend on the concentration of large amounts of energy in a single heavy-current discharge. The apparatus is marked by simplicity and compactness, which allows the use of much larger units than in the earlier apparatus. Of these processes the most important are the Birkeland-Eyde, the Schönherr, and the Pauling.

The Birkeland-Eyde Process.^{3, 70, 71}—The principle on which the Birkeland-Eyde furnace depends is as follows. If a direct-current arc is burned between electrodes which are placed in the field of a powerful direct-current electromagnet, so that the direction of the magnetic field is perpendicular to that of the arc, then the arc moves in a direction at right angles to the magnetic lines of force. The ends of the arc retreat along the electrodes and the path of the arc assumes a semi-circular form. As the arc lengthens its resistance increases, and the voltage rises until a new arc strikes across between the electrodes. Owing to the smaller resistance of the short arc the voltage sinks, and the long arc is finally extinguished when the tension is no longer able to maintain it. The same process is repeated with the new arc, and so on. We thus get a series of arcs starting between the electrodes and moving rapidly outwards until they are extinguished, so that the discharge presents the appearance of a thin semi-

circular sheet of flame. If the horizontal electrodes are supplied with alternating current instead of direct, the arc will be deflected upwards when the current passes in one direction, and downwards when in the other. The discharge then presents the appearance of a circular sheet of flame (Fig. 1). To steady the arc it is necessary to have an inductive resistance in series with it. The Birkeland - Eyde furnace consists of a sheet-steel chamber in the form

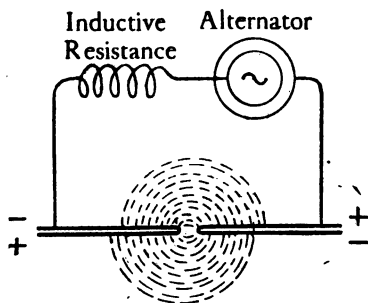


FIG. 1.,

of a low, wide cylinder resting on its side. This is lined internally with fire brick so as to leave a narrow disc-shaped space in the centre about 2 m. in diameter and 5-10 cm. wide. The electrodes enter this space radially, one from each side, along a horizontal diameter, whilst the poles of the large electromagnet are set in the axis of the cylinder, embedded in the refractory lining, so that the direction of the magnetic field is perpendicular to the plane of the central space. The electrodes are copper tubes, cooled by water circulation, and are

placed about 1 cm. apart. They are supplied with alternating current at ca. 5000 volts and 50 periods per second, whilst the coils of the electromagnet are supplied with direct current. The flame sheet produced is about 1.8 m. in diameter. A current of air is driven through the furnace by a Root blower. It enters the flame-chamber from both sides through perforations in the refractory lining, passes radially along the flame and leaves by a peripheral channel in the furnace lining. Fig. 2 shows a section of the later type of furnace; the arrows indicate the direction of the air current. Furnaces taking up to 3000-4000 kilowatts are in operation, and the use of even larger units is contemplated.

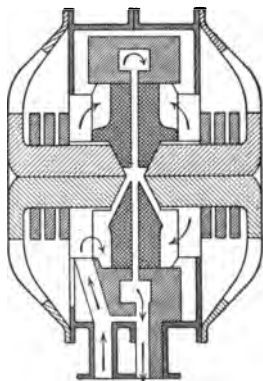


FIG. 2.

The electrodes are changed for repair after about 300 hours' use. This can be rapidly effected. The furnace lining requires attention only once or twice a year, since, in spite of the very high temperature of the flame (ca. 3200°), the walls are kept comparatively cool by the air current.

The gas current leaving the furnace has a temperature of 800° - 1000° , and contains 1-1.5 per cent. NO. It is led first into a large iron main lined with fire-brick, which passes into an aluminium main. This leads to a large vat, where the single main divides into a large number of small aluminium tubes, thus

exposing a large cooling surface. Water is heated or solutions evaporated in the vat by the heat of the gases. The gas leaving the vat is collected in a single main leading to the boiler-house, where the hot current is passed through tubular boilers and raises large quantities of steam, which can be used for evaporation, etc. The gas leaving the boilers has a temperature of about 200°C . It is cooled to about 50°C . by being passed through a series of aluminium tubes over which cold water is flowing. It then enters the oxidation chambers, two large iron cylinders lined with acid-proof material. Here the rate of flow of the gases is checked and time given for the completion of the oxidation of NO to NO_2 . This is necessary, as with dilute gases the time required for complete oxidation is considerable. Thus a mixture of air with 2 per cent. NO requires about twelve seconds for the oxidation of 50 per cent., and one hundred seconds for the oxidation of 90 per cent. of the NO . By means of powerful fans the gas from the oxidation chambers is sent to the absorption towers, enormous granite towers filled with fragments of quartz and provided at the top with an arrangement for distributing the absorbing liquid. In these towers the NO_2 is converted to HNO_3 by the action of water and excess of air (p. 39). A series of three such towers is used at Notodden. The gas traverses the three towers in succession, entering at the bottom and leaving at the top. The absorbing liquid is sent in the opposite direction. When the HNO_3 in the third tower has reached its maximum concentration it is transferred

to the second and replaced by water. The liquid from the second tower goes to the first, the solution being raised from the bottom of one tower to the reservoir at the top of the next by compressed air. The acid leaving the first tower has a concentration of 40-50 per cent., and in the succeeding towers it is more and more dilute. The acid from the first tower is stored in large granite reservoirs. The gases leaving the last acid tower still contain oxides of nitrogen—up to 20 per cent. of the original NO. These are absorbed by alkaline liquids in one or more alkali towers, the absorption by alkali being much more rapid and complete than with water. The wooden alkali towers are filled with brick, and the product obtained depends on the conditions of absorption. If the NO is allowed sufficient time for more or less complete oxidation to NO_2 in its passage from the last acid tower to the alkali tower, a mixture of approximately equal proportions of nitrate and nitrite results. Formerly milk of lime was used as absorbent, and the resulting nitrate-nitrite mixture was decomposed by HNO_3 , giving pure $\text{Ca}(\text{NO}_3)_2$ and oxides of nitrogen, which were returned to the acid towers. At present Na_2CO_3 or NaOH solution is used as absorbent. Insufficient time is given for complete oxidation of the NO, so that a mixture of NO and NO_2 enters the alkali towers. A solution of NaNO_2 is thus obtained (p. 43), which is evaporated, crystallised, and the nearly pure nitrite crystals dried in a centrifugal machine. The gas leaving the alkali towers still contains small quantities of oxides of nitrogen (about 2 per cent. of

the original NO), and these at present are lost. The arrangements for absorption are practically the same in all the factories, although differences in detail occur.

The HNO_3 from the first tower is utilised in various ways. Much of it is converted into calcium nitrate by neutralisation with limestone. The resulting solution is evaporated by the waste heat from the furnace gases until the temperature reaches ca. 140°C . The solution is then allowed to solidify. The solid contains about 80 per cent. anhydrous $\text{Ca}(\text{NO}_3)_2$, or about 13 per cent. N_2 , and is used as a manure (nitrate of lime, air saltpetre, Norwegian saltpetre). Owing to the hygroscopic nature of the neutral nitrate, which is against its use as a manure, various attempts were made to overcome the difficulty. For a time the partly dehydrated neutral nitrate was mixed with a certain proportion of $\text{Ca}(\text{OH})_2$. This gave a fertiliser which was but slightly hygroscopic. The use of the basic nitrate seems, however, to have been abandoned. If the solution of $\text{Ca}(\text{NO}_3)_2$ is evaporated until the temperature reaches 120°C ., it gives on crystallisation pure $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, which is used in the preparation of $\text{Ba}(\text{NO}_3)_2$, large quantities of which are required for the manufacture of fireworks and of barium peroxide. Much of the nitric acid produced by the Birkeland-Eyde process is used in the preparation of $(\text{NH}_4)\text{NO}_3$, by the neutralisation of the HNO_3 with ammonia-water, brought direct from Britain.

The Pauling Process.^{71, 72}—In the furnace invented by H. and A. Pauling the hollow, cast steel, water-

cooled electrodes *a* (Fig. 3) are set at an angle] of 90°. At the lowest point they are about 4 cm. apart, so as not to interfere with the air blast from the nozzle *e*. Through vertical slits in the lowest part of the electrodes thin iron blades *b* are inserted. These so-called "kindling blades" or "ignition knives," the ends of which are only 2-3 mm. apart, serve to start the arc, which is maintained by a high-tension alternating current. The very thin blades do not interfere with the air blast. At each half

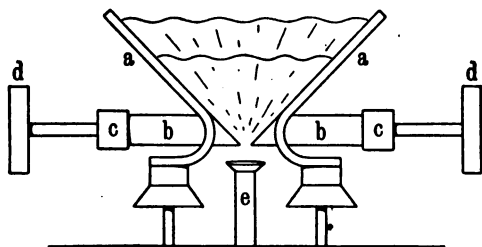


FIG. 3.

period a new arc is formed, which, in consequence mainly of the blast of heated air from *e*, runs along the divergent electrodes until it is extinguished. It is followed by others in rapid succession, so that the result is a continuous sheet of flame about 3 ft. high. The distance between the ignition knives is constantly adjusted by the mechanism *c d* as they burn away. They last about twenty hours and can be rapidly replaced. The main electrodes last about two hundred hours. Two such arcs in series are contained in each furnace, which is made of refractory material. Fig. 4 shows two sections of such a

furnace in directions at right angles to each other. Air enters by A, and the mixture of air and NO leaves by the common outlet B. Through the hollow dividing wall C between the two arcs, cold air which has already been through the furnace is sent into the upper part of the flame. It serves to rapidly cool the gases from the flames without diluting them, and as it enters at a lower pressure than the main

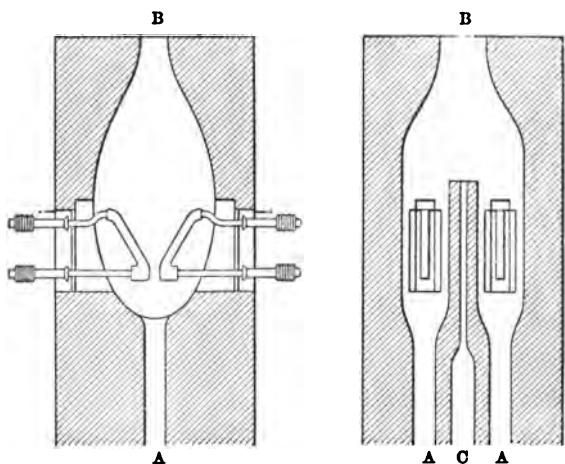


FIG. 4.

current which passes the arcs, it helps to heighten and broaden the flame by its suction effect. The gases leaving the furnace by B have a temperature of about 1000° , and contain 1.15-1.5 per cent. NO. They are used to preheat the entering air, and then pass to two large cooling towers filled with fire-brick. When the bricks in one tower have become sufficiently hot, the current is switched to the second

tower, whilst the first is cooled by drawing a current of fresh air through it. The gases then pass through an aluminium cooler to the oxidation chambers. Part of the gas from the oxidation chambers is returned to the furnaces for cooling purposes, and the rest is sent to the absorption towers, which are arranged on the same principle as that described under the Birkeland-Eyde process. There are five acid towers, giving finally 40 per cent. HNO_3 . The last traces of oxides of nitrogen are absorbed by Na_2CO_3 or NaOH in alkali towers, and the solution obtained gives on concentration nearly pure NaNO_2 . The yield by the Pauling process is about 60 grams HNO_3 per K.W.H. Furnaces with 400 and 600 kilowatt capacity are in operation, and the installation of 1000 kilowatt furnaces is contemplated. The Pauling process is in operation in Austria, Italy, and France.

The Schönherr Process.⁷³—In 1905 Schönherr, of the Badische Anilin-und Soda-Fabrik, with the co-operation of the engineer Hessberger, succeeded in devising a furnace of very simple construction. He found that a stable arc of great length could be maintained in the axis of a tube along which a current of air is passed. The stability of the arc is increased by imparting to the air a whirling motion, so that in their passage along the tube the air particles follow a spiral path. The principle of the furnace differs from that of the two types just described, in which the air current is introduced at right angles to the direction of the discharge, so as to give short contact with the heated area. In the

Schönherr furnace the air current passes along the arc and surrounds it, and is thus in contact with the arc for an appreciable time. In spite of this the concentration of NO in the furnace gases is higher than in either of the other two types of furnace—a result which is explicable by the electrical theory of NO formation. The construction of the furnace is shown diagrammatically in Fig. 5. One electrode is insulated from the rest of the furnace, and consists of a water-cooled copper block through which passes an iron rod E. This rod forms the actual electrode from which the arc starts, and as it wears away can be pushed up. The inner iron tube A forms the actual reaction chamber, and is surrounded by a series of concentric tubes by means of which the entering air is preheated by the hot gases leaving the furnace. The path of the air is evident from the figure.

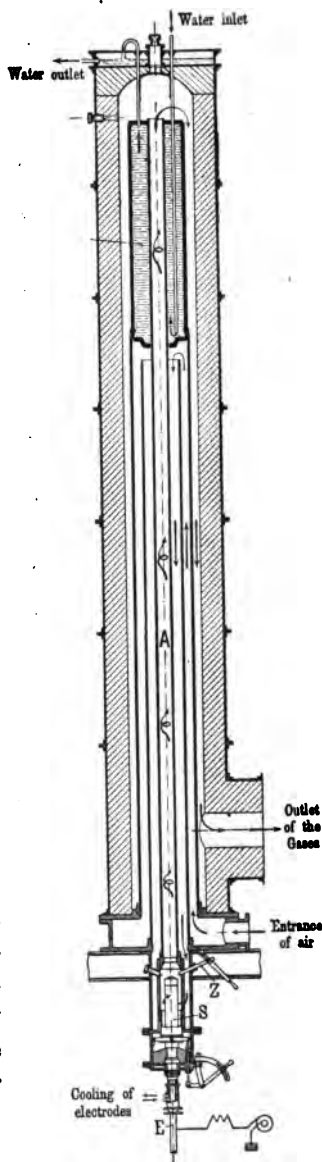


FIG. 5.

The reaction tube forms the second electrode, and is earthed to prevent danger to the operator. The air is admitted to the reaction chamber by a series of rows of tangential openings at the bottom of the tube. A rotary motion is thus imparted to the air current. The admission of air can be regulated by a movable sleeve by means of which the number of openings can be varied. The arc is started by bringing an iron bar, actuated by the lever Z, in momentary contact with the electrode E. The arc is then carried up the tube by the air current, and by suitable manipulation of the air-regulating valve is made to end on the upper water-cooled part of the reaction chamber. In the technical furnaces arcs up to 21 ft. long are employed. The wear of the apparatus is exceedingly slight. The iron electrode E must be renewed about four times a year. This is rapidly done by screwing a new rod to the end of the old one. The wear of the cooler, where the arc ends, is also slight, as the end of the arc is continually changing its position, so that no part gets overheated. The cooler is also so constructed that it can be readily replaced. A constant interchange of gases between the intensely hot layer next the arc and the outer cooler layer is brought about by diffusion and eddy currents. The NO formed is thus rapidly cooled and preserved. The gases leaving the reaction chamber have a temperature of about 1200° , which is reduced to about 850° by preheating the entering gases. They contain 2.25 per cent. NO. The heat of the gases leaving the furnace is utilised in much the same way as in

the Birkeland-Eyde process for evaporating solutions, heating water, and raising steam. Schönherr states that of the total energy supplied about 40 per cent. appears as hot water, and 30 per cent. as steam; 17 per cent. is lost by radiation, and 10 per cent. by cooling with water. Only about 3 per cent. is actually used in the production of NO . Similar figures probably apply to the Birkeland-Eyde and Pauling processes. The yield is about 70 grams HNO_3 per K.W.H. The capacity of the furnaces in use varies from 440-800 kilowatts.

At the Christiansand factory the furnace gases are cooled to about 300°C ., when they contain approximately equimolecular proportions of NO and NO_2 . By absorption with hot NaOH they give practically pure NaNO_2 . In the other factories the NO is transformed into HNO_3 in much the same way as described under the Birkeland-Eyde process. The Birkeland-Eyde and Schönherr interests are now combined, and several large factories are in operation in various parts of the Scandinavian peninsula.

For the concentration of the 40-50 per cent. HNO_3 obtained from the absorption towers various methods have been proposed.⁷⁴ It may be concentrated to about 60 per cent. by the waste heat from the furnace gases. In the factories employing the Pauling process, where the chief product is HNO_3 , the 60 per cent. acid is concentrated by mixing it with 92 per cent. H_2SO_4 , and spraying the mixture into a tower filled with fragments of lava. The tower is heated externally. Nitric acid vapour escapes from the top of the tower and is condensed

to 98 per cent. HNO_3 , whilst 80 per cent. H_2SO_4 flows from the bottom and is concentrated and used again. An electrolytic method of concentration has also been proposed by Pauling,⁷⁵ but does not appear to be in use.

Distillation with phosphoric or arsenic acids, or with polysulphates ($\text{Na}_2\text{H}(\text{SO}_4)_2$), and dehydration with anhydrous $\text{Ca}(\text{NO}_3)_2$ and subsequent distillation, are some of the numerous methods patented for the concentration of the nitric acid.

An exhaustive account of the utilisation of Scandinavian water-power in the air-nitrate industry, and of its financial and commercial organisation, is given by Norton.⁴

Synthesis of Nitric Oxide by Non-electrical Means.—It has already been pointed out that small quantities of oxides of nitrogen are produced by the explosion of such gases as carbon monoxide¹⁵⁰ or hydrogen¹⁵¹ with air, or by their combustion in air, especially under pressure. Various methods¹⁵² based on these or similar reactions have been proposed for the production of nitric acid from air. Whilst some of them are quite sound in principle, none of them has so far met with any measure of technical success.

Oxidation of Ammonia to Nitric Acid and Nitrous Acid.—Although at present the direct oxidation of atmospheric nitrogen is apparently the most economical means of preparing nitric acid from the air, it must be borne in mind that methods for the production of NH_3 from atmospheric nitrogen are being rapidly perfected. Should it be found that atmospheric nitrogen can be more economically fixed

as NH_3 than as HNO_3 , methods for the oxidation of NH_3 to HNO_3 will assume technical importance. Indeed, such an eminent authority as Dr Rudolph Messel has expressed the opinion⁷⁶ that, so long as the production of HNO_3 from air is confined to countries where cheap water-power is available, and the difficulties attending the transport of HNO_3 remain, methods for the oxidation of NH_3 to HNO_3 deserve more attention than they have hitherto received. Ammonia is obtainable locally everywhere, either as a by-product from the manufacture of illuminating gas, Mond gas, or coke, and it may in future be produced sufficiently cheaply by any of the numerous processes now on trial for the production of NH_3 from atmospheric nitrogen.

A great many methods for effecting the oxidation have been proposed.⁷⁷ Here, however, we need consider only the oxidation by atmospheric oxygen in presence of catalytic agents. Kuhlmann⁷⁸ found that on passing a mixture of air and ammonia over heated spongy platinum, nitric and nitrous acids were produced. Later investigations showed that many other metals and metallic oxides had a similar catalytic effect, but the best results are secured by the use of platinum.

Ostwald and Brauer⁷⁹ studied the catalytic oxidation with a view to its technical application. They found that the best catalyst was sheet platinum with a certain proportion of spongy platinum on its surface. When a mixture of ammonia and excess of air was led over the catalyst heated to redness, 85 per cent. of the theoretical yield of HNO_3 was

obtained under the most favourable conditions. The rest of the nitrogen escaped as free nitrogen. According to Ostwald and Brauer, the reaction takes place in stages, the intermediate products being oxides of nitrogen, and the final products nitrogen and water. They aim at preserving the intermediate products as much as possible. The velocity with which the gases are passed over the catalyst is, therefore, of the greatest importance. They find that spongy platinum alone is too vigorous a catalyst, since it decomposes the oxides of nitrogen too rapidly. The technical details were gradually perfected, and in 1909 a factory was equipped at Gerte, Westphalia. Great secrecy is maintained with regard to the details of the process, owing to the absence of patent protection in Germany, but the oxides of nitrogen are worked up to nitric acid in much the same way as in the direct oxidation of nitrogen. The nitric acid produced is mainly converted into ammonium nitrate by neutralisation with ammonia.

Schmidt and Böcker⁵⁵ also studied the oxidation of NH_3 by air, using platinum or platinum asbestos as catalyst. They obtained up to 80 per cent. of the NH_3 as oxides of nitrogen, and showed that the first product of the oxidation was NO , which, however, was rapidly oxidised to N_2O_3 .

Fr. Bayer & Co.,⁸⁰ using burnt pyrites (ferric oxide with a little copper oxide) as catalyst, and working at $600^\circ\text{--}750^\circ$, obtained N_2O_3 as the sole product of the oxidation; by absorption with alkali this was converted into alkali nitrite.

Frank and Caro⁸¹ found that by using thorium

oxide or a mixture of this with other rare earth oxides as catalyst, NH_3 could be oxidised by air at $150^\circ\text{--}200^\circ$, with a yield of 90 per cent. of HNO_3 or HNO_2 .

Oxidation by Nitrifying Bacteria.—Interesting results have been obtained by Müntz and Lainé⁸² in their endeavours to utilise nitrifying bacteria for the oxidation of ammonia to nitric acid on a large scale. They find that the best medium is peat. This is impregnated with sufficient lime to combine with the nitric acid formed, and inoculated with the bacteria. A dilute solution of $(\text{NH}_4)_2\text{SO}_4$ (0.75 per cent.) is allowed to trickle through the mass, and a nearly 1 per cent. solution of $\text{Ca}(\text{NO}_3)_2$ is obtained. Only dilute solutions of $(\text{NH}_4)_2\text{SO}_4$ undergo quick nitrification, but as the presence of even 22 per cent. nitrate in the solution does not interfere with nitrification, more $(\text{NH}_4)_2\text{SO}_4$ can be added to the dilute nitrate solution, which can then be again subjected to the action of the bacteria. Proceeding in this way, Müntz and Lainé obtained a solution containing 41.7 grams nitrate per litre by passing the solution five times through the peat, and even then the limit was not reached. The most favourable temperature is 30°C . The yield obtained was 6.5 kilos. of calcium nitrate in twenty-four hours per cubic metre of peat, compared with about 5 kilos. of crude saltpetre in two years per cubic metre of the old "saltpetre plantations."

SECTION II.

SYNTHESIS OF AMMONIA AND AMMONIUM COMPOUNDS FROM ATMOSPHERIC NITROGEN.

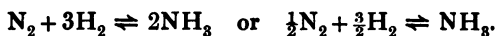
The Equilibrium between Nitrogen, Hydrogen, and Ammonia. — It has long been known that ammonia, which is quite stable at ordinary temperature, breaks up into its elements on heating. Thus Priestley observed the decomposition of the gas on passing it through a red hot glass tube. Other investigators confirmed the decomposition, but obtained very varying results as to the degree of decomposition, which was found to depend largely on the nature and extent of the surface in contact with the gas. The catalytic effect of different substances and the influence of a large surface of contact are well illustrated by the experiments of Ramsay and Young,⁸³ who showed that in iron or porcelain tubes, or in glass tubes filled with asbestos, the decomposition commenced at ca. 500° C. and was practically complete at 780°, whilst in glass vessels alone the decomposition did not begin until ca. 780°. They further showed that the observed degree of decomposition depended very largely on the velocity with which the NH_3 was passed through the heated tube.

Ammonia is also decomposed under the influence of electric sparks, and it was generally held that

the decomposition was complete on prolonged sparking. Deville⁸⁴ showed, however, that even on prolonged sparking a trace of ammonia remained undecomposed, and he thus demonstrated the reversible nature of the reaction.

The reverse reaction, the synthesis of NH_3 from its elements under the influence of the electric spark, was also early observed and repeatedly confirmed. The union took place only to a limited extent, unless the NH_3 formed was removed, *e.g.* by combination with an acid, as fast as it was formed. A summary of the earlier work on the subject is given by Gmelin-Kraut⁸⁵ and by Abegg.⁸⁶

These facts are explained as follows. The reaction between nitrogen and hydrogen leads to an equilibrium according to the equation—



At equilibrium the following relation holds:—

$$\frac{p_{\text{NH}_3}}{p_{\text{N}_2}^{\frac{1}{2}} \times p_{\text{H}_2}^{\frac{3}{2}}} = K_p,$$

where p_{NH_3} , p_{N_2} , and p_{H_2} are the partial pressures of NH_3 , N_2 , and H_2 respectively at equilibrium and K_p is the equilibrium-constant. The concentration of NH_3 present at equilibrium depends on the temperature and pressure. For a given temperature and pressure the proportions of the three gases present at equilibrium should, of course, be the same, whether we start with a mixture of nitrogen and hydrogen in the proportions demanded by the equation or with pure NH_3 .

The union of nitrogen and hydrogen to ammonia is an exothermic reaction, and, at ordinary temperature, is accompanied by an evolution of 11,890 cal. per gram-mol. of NH_3 ; the concentration of NH_3 at equilibrium must, therefore, diminish with increasing temperature. To obtain a high concentration of NH_3 at equilibrium, therefore, the temperature must be kept as low as possible. On the other hand, the velocity with which the equilibrium is reached decreases with decreasing temperature, so that unless a suitable catalyst is available it may be impossible to reach the equilibrium at low temperatures.

Since the combination of nitrogen and hydrogen to NH_3 is accompanied by a diminution of pressure at constant volume, increase of pressure will increase the concentration of NH_3 at equilibrium for a given temperature.

The first systematic investigation of the equilibrium by modern methods was made by Haber and van Oordt.⁸⁷ They used iron and nickel as catalysts, and worked at ca. 1000°C . and at atmospheric pressure. The equilibrium was reached from both sides by the following ingenious arrangement. Pure dry NH_3 was passed through a porcelain tube, which contained the catalyst, heated in an electric furnace. The NH_3 was absorbed from the issuing gases by H_2SO_4 , and the remaining mixture of 1 vol. N_2 and 3 vols. H_2 passed through another porcelain tube containing catalyst lying alongside the first in the furnace. The NH_3 formed by the union of N_2 and H_2 in this second tube was also absorbed by H_2SO_4 .

The volume of the residual nitrogen and hydrogen was measured and the NH_3 formed in the two H_2SO_4 flasks determined by titration. From these data the concentration of NH_3 at equilibrium at the temperature of the furnace was determined. At 1020°C . they found 0.012 per cent. by volume NH_3 at equilibrium, but they claim no great accuracy for this result. It showed, however, that at high temperatures, where the equilibrium is rapidly reached, the position of the equilibrium is very unfavourable for the technical synthesis of NH_3 .

A more accurate investigation of the NH_3 equilibrium was carried out by Haber and Le Rossignol.⁸⁸ They used iron, manganese, nickel and chromium as catalysts, but even with iron and manganese, the best catalysts, it was only above 750°C . that the equilibrium was reached quickly, and at this temperature the NH_3 is almost completely dissociated. They worked at atmospheric pressure and retained the method employed by Haber and v. Oordt, with certain improvements in detail. The general results of Haber and v. Oordt were confirmed. The following table gives the results of the investigation:—

Temp. C.	$10^4 \times K_p$	Per cent. NH_3 at equilibrium.
1000	1.48	0.0048
930	2.00	0.0065
850	2.79	0.0091
800	3.34	0.0109
750	4.68	0.0152
700	ca. 6.8	ca. 0.0221

The concentrations of NH_3 (per cent. by vol.) are for a gas mixture containing 3 vols. H_2 and 1 vol. N_2 at atmospheric pressure.

From the equilibrium equation (p. 62) it can be shown that the denominator, and consequently also the numerator, is a maximum when the partial pressure of H_2 is three times the partial pressure of N_2 , *i.e.*, when the gases are present in the proportions demanded by the equation $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$. The maximum concentration of NH_3 at equilibrium for a given temperature and pressure will, therefore, be obtained when the H_2 and N_2 are present in these proportions.

From the equilibrium determined at these high temperatures, the concentration of NH_3 for equilibrium at lower temperatures was calculated by means of the formula—

$$\text{Log}_{10} K_p = \frac{2215}{T} - 3.626 \log_{10} T + 3.07 \times 10^{-4} T + 2.9 \times 10^{-7} T^2 + 4.82,$$

which takes into account the variation of the heat of the reaction with temperature. At 327°C . the equilibrium mixture should contain 1.67 per cent. NH_3 , and at 27°C . 96.32 per cent. NH_3 . It is, therefore, evident that a good yield of NH_3 could be obtained at low temperatures if a suitable catalyst were found.

Nernst,⁸⁹ from theoretical considerations, and Jost,⁹⁰ from the result of experiments on the NH_3 equilibrium carried out under pressures up to 70 atmos., conclude that the equilibrium-concentrations

obtained by Haber and his co-workers are too high. They attribute the difference between their results and Haber's to the difficulty in determining the small amounts of NH_3 formed under atmospheric pressure. The greater concentrations of NH_3 obtained under high pressure can be much more accurately determined.

Haber and Le Rossignol,⁹¹ therefore, undertook a fresh determination of the equilibrium at a total pressure of 30 atmos. They used a narrow quartz tube as reaction-chamber and Fe and Mn as catalysts, and took all precautions to eliminate errors. The equilibrium was attained from both sides, and good agreement obtained between the figures from the synthesis and the decomposition. Their results were as follows:—

Temp. C.	Per cent. NH_3 at equilibrium.	$10^4 \times K_p$.
700	0.654	6.80
801	0.344	3.56
901	0.207	2.13
974	0.144 to 0.152	1.48 to 1.56

The relation between the results at 30 atmos. and at 1 atmos. can be deduced as follows:—If P is the total pressure, and c is the fraction which each gas forms of the total volume at equilibrium, then—

$$P \times c_{\text{NH}_3} = p_{\text{NH}_3}, \quad P \times c_{\text{N}_2} = p_{\text{N}_2}, \quad P \times c_{\text{H}_2} = p_{\text{H}_2},$$

and we get from the equilibrium equation (p. 62)—

$$\frac{c_{\text{NH}_3}}{c_{\text{N}_2}^{\frac{1}{2}} \times c_{\text{H}_2}^{\frac{3}{2}}} = K_p \times P.$$

So long as the NH_3 concentrations are small, which is the case in the temperature interval investigated both at 1 atmos. and at 30 atmos., the product $C_{\text{N}_2}^{\frac{1}{2}} \times C_{\text{H}_2}^{\frac{3}{2}}$ will be practically constant. In this case it is evident from the above equation that, for a given temperature, the NH_3 concentration at equilibrium will be proportional to the total pressure. NH_3 concentrations at 1 atmos. should be, therefore, about $\frac{1}{30}$ of those at 30 atmos. for the same temperature. On this assumption the agreement between the results at 30 atmos. and the previous results at 1 atmos. is excellent. Haber and Le Rossignol, therefore, maintain the accuracy of their equilibrium determinations, and conclude that in Jost's experiments the equilibrium from the synthetic side was not reached.

Technical Synthesis of Ammonia.—Haber and Le Rossignol next took up the question of the technical synthesis of NH_3 and, with the co-operation of the Badische Anilin-und Soda-Fabrik, succeeded in devising a process which seems to offer a satisfactory solution of the problem. A short account of the experimental apparatus used is given by Haber,⁹² and a detailed account of the apparatus, and of experiments with various catalysts by Haber and Le Rossignol.⁹³ We may here summarise the conditions most favourable for the technical synthesis of NH_3 , as deduced from the investigations just discussed. The most favourable mixture of N_2 and H_2 is 1 vol. N_2 to 3 vols. H_2 . With this mixture the maximum concentration of NH_3 attainable is greater the lower the temperature, whilst for a given

temperature the equilibrium concentration of NH_3 is higher the higher the total pressure. This is illustrated by the following table, which gives the calculated percentage by volume of NH_3 at equilibrium for different temperatures and pressures:—

Temp. C.	1 atm.	100 atm.	200 atm.
500	0.13	10.7	18.1
550		7.0	12.2
600	0.048	4.5	8.3
650		3.0	5.8
700	0.021	2.1	4.1

The lower the temperature, however, the smaller is the velocity of the reaction, and, therefore, the longer the time required for equilibrium to be reached. But in a technical process not only the concentration of NH_3 attainable, but also the time taken to attain it, must be considered. The most active catalyst for the reaction must, therefore, be found, so as to enable the reaction to be carried out sufficiently rapidly at as low a temperature as possible.

Haber and Le Rossignol find that with the best catalysts at present known it is difficult to work below 500°C . On the other hand, it is unnecessary to go above 700°C ., since with these catalysts the equilibrium is practically reached at this temperature, even when the velocity of passage of the gases over the catalyst is considerable.

In their work on the technical synthesis of NH_3 , Haber and Le Rossignol used pressures up to 200 atmos. The difficulties in constructing apparatus, and especially a reaction-chamber to withstand such

pressures at the temperatures employed, were great, but were brilliantly overcome. Various experimental furnaces were used, according to the temperature and pressure employed. For lower temperatures (500°-

600°) a very simple furnace could be used. It consisted of a strong steel cylinder containing the catalyser, tightly closed with a cap. The cap was provided with a steel capillary inlet-tube for the gases, reaching to the bottom of the cylinder, and a steel capillary exit-tube. The heating was external. For higher temperatures, above 700°, the use of metal vessels which have to stand a high internal pressure is doubtful. Fig. 6 shows diagrammatically the essential principles in the design of the furnaces for such temperatures, although several furnaces varying in details of construction were employed. The reaction-chamber consists of a thin iron tube A wrapped in asbestos and wound with nickelin wire C as heating resistance.

Into the iron tube passes a glass or quartz tube B, which is narrowed towards the lower end and contains the catalyst between asbestos plugs

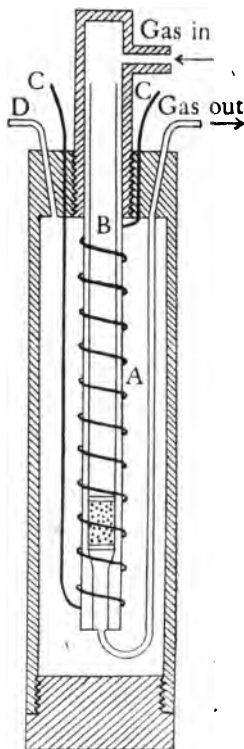


FIG. 6.

at this point. The gases enter the glass tube and leave at the bottom of the iron tube. The heated thin-walled iron tube would not stand a pressure of 100-200 atmos. without deformation, unless the external pressure were also kept high. It is, therefore, surrounded by a much stronger steel tube, and a high pressure maintained in the space between the two by means of the auxiliary pressure-tube D. The space between the inner and outer tubes is filled with heat-insulating material. The arrows show the direction in which the gas passes. In the larger furnaces the hot gases leaving the reaction-chamber are, by suitable arrangements, made to give up their heat to the fresh gases entering the apparatus.

With such furnaces the effect of various catalysts was investigated under varying pressures, and with varying velocity of passage of the gases. The N_2 - H_2 mixture (1:3) was freed from oxygen and moisture and passed through the furnace, the temperature of which was determined by thermocouples in the inner tube. The greater part of the NH_3 in the gas issuing from the furnace was liquefied and measured in a suitable condensing tube. The gas leaving the condensing tube still contained some NH_3 (the amount depending on the temperature of the liquefying chamber), which was determined either by a gas-interferometer²⁴ or by titration. Of the catalysts tried, namely Ce, Mn, W, Ur, Ru, Os, by far the most effective were Os and Ur. It is noticeable that in both the Fe and Cr groups, the metals of highest atomic weight are far more

effective catalysts than those of lower atomic weight. The world's supply of Os is so small, however, as to preclude its use in technical work. With Ur the following results were obtained. At 600° C. and 190 atmos., with a gas velocity of 20 litres per hour, the gas contained 5·8 per cent. NH_3 . At 580° C., 190 atmos. and 3 litres per hour, over 7 per cent. NH_3 . At 580° C., 120 atmos. and 3 litres per hour, 4·8 per cent. NH_3 ; 20 litres per hour, 3·5 per cent. NH_3 . At 610° C., 155 atmos., 3·80 per cent., 5·05 per cent., and 5·50 per cent. NH_3 was obtained, with velocities of 10, 5, and 3 litres per hour respectively. At 117 atmos., 9·1 per cent. NH_3 was obtained with 9·5 litres per hour at 490° C., 11 per cent. NH_3 with 2 litres per hour at 508°, and 11·9 per cent. NH_3 with 2 litres per hour at 493°. These are lower than the equilibrium-concentrations, as the velocity was too great to allow equilibrium to be reached. From the table (p. 68) it will be seen that in no case is the concentration of NH_3 so high that it would pay simply to absorb the NH_3 from the reaction products and allow the residue to go to waste. A continuous process must, therefore, be adopted. The NH_3 formed by the passage of the gases over the catalyst must be removed and the uncombined gases again subjected to the action of the catalyst, after the addition of fresh N_2 and H_2 to replace that removed as NH_3 , as it is advantageous to keep up the pressure. Under the high pressure employed, the removal of the NH_3 by condensation at a low temperature is a particularly simple process. For this purpose temperatures down to -75°C. may be safely employed.

Below this temperature there is risk of stoppage of the gas passages by solidification of the NH_3 . However low the temperature used for the condensation of the NH_3 , there is always some NH_3 in the gases leaving the condensing-chamber, the amount corresponding to the vapour pressure of liquid NH_3 under the working conditions. This amount is higher for a given temperature in presence of a compressed foreign gas than over the pure liquid itself.

In an experiment with gas circulation to test the technical possibilities of the process the following arrangement was used. By means of a small double-acting pump the dry $\text{N}_2\text{-H}_2$ mixture was sent through the furnace, which contained Os as catalyst. The gases leaving the furnace were dried by soda-lime and then passed through a system of copper capillaries enclosed in a strong steel cylinder, the arrangement constituting a "cold regenerator." The gases then passed to the liquefier, where the greater part of the NH_3 was condensed by passing through a coil immersed in a mixture of solid CO_2 and ether, which maintained a temperature of about -30°C . From the liquefier the gases passed to the outer steel chamber of the "cold regenerator" and thence to the pump. In the "cold regenerator" the cold gases from the liquefier on their way to the pump are used to cool the warm gases entering the capillaries before these reach the liquefier. Between the pump and the furnace is a valve by which fresh $\text{N}_2\text{-H}_2$ mixture is introduced to replace the NH_3 removed in the liquefier. In an experiment lasting

four hours the apparatus worked with extreme smoothness. With a pressure varying from 193-163 atmos., the concentration of NH_3 varied from 2.4-3.1 per cent. Higher figures would have been obtained with a larger quantity of catalyst. About 336 grams of liquid NH_3 was obtained in the four hours. The heat and cold regenerators worked with surprising efficiency.

The technical synthesis of NH_3 on the lines indicated by Haber has been taken up by the Badische Anilin-und Soda-Fabrik, and Bernthsen⁸⁶ gives a summary of the results obtained. It was found that a number of substances, such as alkali, alkaline earth, and earth oxides, hydroxides and salts, and many metals, have the power of rendering catalysts in general more active. Metals such as Pb, Zn, Sn, Bi, and metalloids such as S, Se, Te, As, B, and P must be avoided, as they act as contact poisons. Mo and many of its compounds are excellent catalysts. Another suitable catalyst is tungsten, either as metal, alloy, or nitrogen compound.

By the brilliant work of Haber and his collaborators the problem of the technical synthesis of NH_3 has been solved, and the process has been so far perfected by the experts of the Badische Fabrik that the first factory for the manufacture of synthetic NH_3 is in course of erection by that company at Oppau, near Ludwigshafen.

A great advantage of the NH_3 synthesis for the fixation of nitrogen is that the amount of energy required for the process is small. The manufacture

of synthetic ammonia would not, therefore, be confined to districts where large amounts of cheap water-power are available, as is the case with the manufacture of nitric acid or of calcium cyanamide from atmospheric nitrogen.

Various Processes for Ammonia and Ammonium Compounds.—Of the numerous other methods which have been from time to time proposed for the conversion of atmospheric nitrogen into ammonia or ammonium compounds, the following may be mentioned. According to De Lambilly,⁹⁶ a mixture of nitrogen, hydrogen, steam and carbon monoxide passed over certain catalysts, especially spongy platinum, gives ammonium formate—



whilst if the CO is replaced by CO₂ ammonium bicarbonate results—



Technically the gases can be obtained by the alternate action of air and steam on white-hot coke. According as bicarbonate or formate is desired, the CO or CO₂ is removed from the gas mixture before subjecting it to the action of the catalyst. The most favourable temperature for the formate formation is 80°-130°, and for the bicarbonate formation 40°-60°.

Schlutius⁹⁷ exposes a mixture of Dowson gas (14 per cent. H₂, 43 per cent. N₂, 39 per cent. CO, 4 per cent. CO₂) and steam to the action of the silent discharge in presence of platinum. Above 80° ammonium formate is obtained, below 80° ammonia.

For an account of various other processes the reader is referred to Donath and Indra,⁹⁸ or to Lunge.⁹⁹

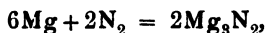
Various inventors¹⁰⁰ have patented processes for the recovery of the nitrogen in peat as ammonia, and have claimed that at the same time a synthesis of ammonia from atmospheric nitrogen takes place under the catalytic influence of the peat. In such processes a mixture of air and steam is passed over peat at 300°-500°. The reaction is capable of furnishing an excellent power-gas, together with various valuable by-products, including NH_3 . Caro¹⁰¹ has shown, however, that it is not possible to obtain a yield of NH_3 greater than corresponds to the combined nitrogen in the peat, so that no synthesis from atmospheric nitrogen takes place. An account of the utilisation of peat for the production of power-gas, ammonia, and other by-products is given by Norton,¹⁰² Donath and Indra,¹⁰³ and by Lunge.¹⁰⁴

SECTION III.

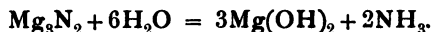
CONVERSION OF ATMOSPHERIC NITROGEN INTO COMPOUNDS WHICH READILY YIELD AMMONIA.

Formation and Decomposition of Nitrides.

MOST metals, and many non-metals, combine more or less readily with nitrogen to form nitrides, from most of which the nitrogen can be obtained in the form of ammonia by treatment with water or alkalies. Thus heated magnesium readily absorbs nitrogen, forming nitride—



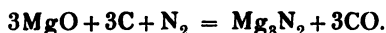
and the nitride is decomposed by water as follows:—



The metals which readily form nitrides are much too dear, however, to allow of such processes being carried out remuneratively on a technical scale. Methods were, therefore, sought by which the nitrides could be prepared from cheap compounds of the metals, or in which the metal could be used as a catalytic agent in the synthesis of ammonia, the nitride formation being an intermediate step in the process. Of the numerous processes which have been proposed, the only one which at present seems

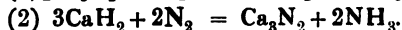
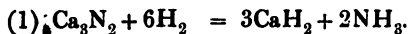
to be in successful technical operation is that depending on the formation of aluminium nitride, AlN . Of the others a few only need be mentioned here. A full account is given by Donath and Indra,¹⁰⁵ by Norton,¹⁰⁶ and by Lunge.¹⁰⁷

Willson¹⁰⁸ and Mehner¹⁰⁹ heat a mixture of magnesia and carbon in a current of nitrogen in an electric furnace—

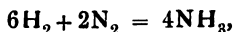


The oxides of other elements which form nitrides at high temperatures, *e.g.*, B, Si, Ti, V, etc., react similarly.

Kaiser¹¹⁰ bases his process on the following reactions:—



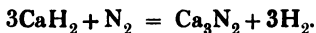
Summing these reactions we obtain—



so that a mixture of Ca_3N_2 and CaH_2 should act as a catalyst in the synthesis of NH_3 . Haber and v. Oordt⁸⁷ have shown, however, that the main reaction when hydrogen is passed over heated Ca_3N_2 is—



only a little NH_3 being formed according to (1). When nitrogen is passed over CaH_2 practically no NH_3 is formed, the main reaction being—



A mixture of Ca_3N_2 and CaH_2 , therefore, catalyses

the synthesis of NH_3 only to a slight extent, and at the temperature required (ca. $800^\circ\text{C}.$) the position of the ammonia equilibrium is too unfavourable for a successful technical process. The catalysis of the NH_3 synthesis by Mn, with intermediate formation of manganese nitride, is somewhat more favourable, but here also the temperature required is too high, and the intermediate reaction too slow.

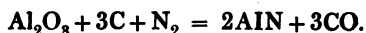
Borchers and Beck¹¹¹ claim to have devised a process of fairly general applicability for the conversion of compounds of many metals into nitrides from which NH_3 can be prepared. A solution of a halide or oxide of the nitride-forming metal in a fused mixture of alkali or alkaline earth halogen salts is electrolysed. As cathode, a layer of molten metal is used, which does not itself form a nitride but readily alloys with the nitride-forming metal. The anodes are of carbon or resistant metal. On electrolysing, the nitride-forming metal is liberated at the cathode and alloys with the cathode metal. The fluid alloy is treated with a current of nitrogen when nitride is formed, which is removed and treated with water or steam. Ammonia is evolved and the hydroxide or oxide of the metal left. After drying, this can be returned to the electrolytic chamber. The metal acts, therefore, practically as a catalyst. The process can be used for the formation of nitrides of Al, Mg, and the alkaline earth metals.

Numerous methods depending on the transformation of oxides and other compounds of B, Si, Ti, and Mo into nitrides or other nitrogen compounds of these elements, and the subsequent decomposition of the

nitrogen compounds by water, acids, or alkalis, have been described and patented. It is, however, impossible to consider them here. An account of them will be found in the sources quoted above. None of them, so far as can be ascertained, have been tried on a technical scale.

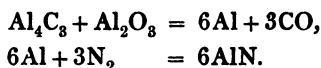
Serpek's Aluminium Nitride Process.—The only process depending on the formation of a metallic nitride which at present seems to offer prospects of technical success is that devised by Serpek, which depends on the production of aluminium nitride from alumina, and subsequent decomposition of the nitride. An account of the development of the process is given by Norton,¹¹² Donath and Indra,¹¹³ and Richards.¹¹⁴ Serpek at first used powdered aluminium carbide as raw material, and heated this in a current of nitrogen or generator-gas. The absorption of nitrogen was said to be increased by the addition of carbon or aluminium to the carbide, and by the presence of traces of SO_2 or HCl in the gas-current. Caro¹¹⁵ showed that the absorption of nitrogen by Al_4C_3 was probably preceded by dissociation of the carbide into aluminium and carbon.

Later a mixture of alumina and carbon (coal) was heated in a current of nitrogen or generator-gas to red heat. The formation of nitride takes place according to the equation—



The addition of 5 per cent. copper or iron facilitated the absorption, and the action of these metals was

regarded as catalytic. In this case also the presence of traces of SO_2 or HCl was said to favour absorption of nitrogen. Serpek assumed that Al_4C_3 was first formed, which then reduced the remaining Al_2O_3 to aluminium, which combined with the nitrogen—



Further investigation showed that the yield of nitride depended greatly on the temperature employed. It was found that some absorption of nitrogen took place even at 1100°C .; at 1500° nitrogen was absorbed fairly rapidly, at 1700° energetically, and at 1800° - 1850° almost violently, giving nearly chemically pure nitride. Smaller yields were obtained at higher temperatures, and above 2000°C . the production of nitride practically ceased, owing to decomposition of the nitride. The most favourable temperature is, therefore, 1800° - 1900° . It was also found that impure alumina, such as bauxite, could be converted into nitride at somewhat lower temperatures than pure, evidently owing to the catalytic effect of the impurities.

The Serpek process is being tested in France on a large scale by the Société Générale des Nitrures, who have acquired all the Serpek patents. The apparatus used is shown diagrammatically in Fig. 7. It consists of two superposed, rotating cylindrical kilns, slightly inclined to one another and rotating in opposite directions. Into the upper one, A, the powdered bauxite is introduced and is calcined in its descent by the passage of the hot gases over it. The calcined

bauxite falls into the funnel B in the chamber D and is there mixed with the necessary carbon, introduced at P. The mixture then enters the cylinder C, and in its descent passes the electrically heated region F, where it is heated to the reacting temperature 1800° - 1900° . The iron cylinder C is lined with compressed nitride. The detachable electrical resistance furnace F is formed of a series of bars

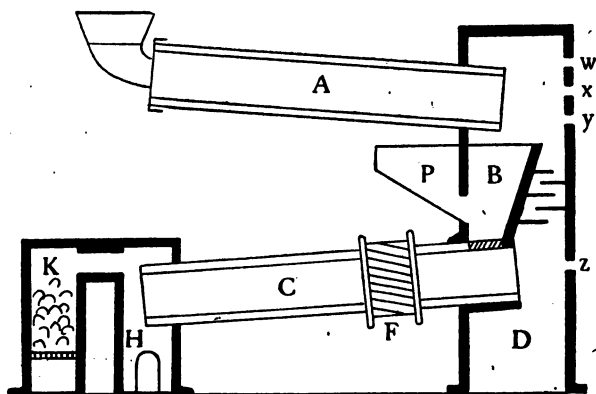
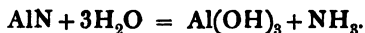


FIG. 7.

of compressed carbon and AlN . These are either embedded longitudinally in the lining of the furnace, or cross the furnace diametrically. Generator gas (ca. 30 per cent. $\text{CO} + 70$ per cent. N_2) is produced in the generator K and enters C at a temperature of ca. 400° . It becomes highly heated in passing through the kiln in the direction contrary to that of the descending charge. In the electrically heated region the nitrogen reacts with the alumina-carbon mixture, giving AlN and CO . The gas, rich in carbon

monoxide, leaving the high temperature zone preheats the descending charge, issues from the upper end of the kiln into the mixing chamber D, where it meets with a blast of air from *w, x, y, z*, which burns the carbon monoxide to carbon dioxide. The heat produced is used to calcine and preheat the bauxite in the upper kiln. The siliceous impurities in the charge are mostly volatilised out, probably as free silicon, which is burned to silica by the air blast. The chamber D is provided with baffle-plates to remove dust from the ascending gases. The nitride formed in C is collected in the air-tight chamber H. The apparatus effects the necessary intimate mixing of the charge and intimate contact of nitrogen with the charge, and at the same time secures a very economical use of the heating current, whilst the heat of combustion of the carbon monoxide, both from the generator and from the reaction, is also utilised. The product from bauxite contains about 26 per cent. N_2 , but by using pure alumina, pure AlN (34 per cent. N_2) can be obtained.

The AlN can be decomposed by water or alkali, giving NH_3 —

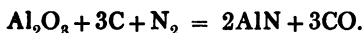


By decomposing the nitride with alkali or with sodium aluminate solution, according to the Bayer process, the nitrogen is recovered as NH_3 , whilst a very pure alumina, free from iron and silica, is obtained. With AlN , too, a much more dilute alkali can be used than is possible in the manufacture of pure alumina from bauxite by the Bayer process.

The pure alumina is suitable for the production of metallic aluminium, or it may be again converted into nitride. The combination of the nitride process with the manufacture of pure alumina for use in the electrolytic production of aluminium, seems to offer an exceptionally cheap source of ammonia.

Scientific Investigation of the Serpek Process.

—Remarkably few scientific investigations of the reaction involved in the Serpek process have appeared. Tucker and Read¹¹⁶ found that the absorption of nitrogen by a mixture of alumina and carbon was very slight below 1600° C., reached a maximum between 1800° and 2000° C., whilst above 2000° decomposition of the AlN seemed to occur. The formation of the nitride takes place according to the equation—

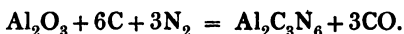


Serpek's statement that bauxite reacts more readily than pure alumina was confirmed, but it was found that the presence of appreciable amounts of SO₂ in the nitrogen was harmful.

An important contribution to the subject was recently made by Fraenkel,¹¹⁷ who gives also a very complete bibliography of the earlier literature on aluminium nitride. Fraenkel studied the velocity of absorption of pure dry nitrogen by a mixture of 2 parts pure alumina and 1 part finely divided pure soot, and found that the velocity of absorption is very small at 1350°, increases moderately up to 1500°, and very rapidly above 1500°. Thus in thirty minutes 0.2 per cent. N₂ was absorbed at

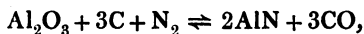
1350°, 3.1 per cent. at 1400°, 4.4 per cent. at 1450°, 8 per cent. at 1500°, 19.5 per cent. at 1550°, and 24.5 per cent. at 1600°. Up to 1500° the amount of nitrogen absorbed is approximately proportional to the time, but at higher temperatures the reaction goes quickly at first, and then, after a large proportion of the charge has reacted, slows down considerably.

According to Peacock and Du Pont¹¹⁸ a mixture of 3 parts of alumina and 1 part of carbon reacts with nitrogen under 500 mm. pressure at 1500° according to the equation—



Fraenkel obtained no indication of such a reaction, but found that at pressures down to 250 mm. the velocity of the reaction was practically the same as at atmospheric pressure.

A different result is obtained if the partial pressure of the nitrogen is lowered by mixture with another gas, especially CO, the product of the reaction. If we regard the reaction—



as reversible, the law of mass-action gives $C_{\text{N}_2}/C_{\text{CO}}^3 = K$. The reversibility of the reaction was proved by passing different mixtures of N_2 and CO at a given temperature either over a mixture of alumina and carbon, or over a mixture containing a certain proportion of AlN, and determining the percentage of nitrogen in the mixture before and after passing the gas. When the proportion of CO in the gas

mixture was above a certain amount, the percentage of nitrogen in the solid diminished, showing that the reaction from right to left was taking place. When the proportion of CO was below a certain amount, nitride formation took place. The results show distinctly that an equilibrium exists, but it was not possible to define it accurately. At a total pressure of 1 atmos. the equilibrium concentration of CO at 1500° is between 25 per cent. and 40 per cent. CO, and at 1600° between 50 per cent. and 65 per cent. CO. At 1700° active absorption of nitrogen still took place from a gas containing 70 per cent. CO. With increasing temperature the equilibrium concentration of CO, therefore, increases. This result is important technically. If generator gas is used, a higher temperature is required than with pure nitrogen, and the higher the temperature the less pure does the nitrogen require to be. Further, with generator gas it is useless to look for catalysts for the reaction in the neighbourhood of 1500°. These can be effective only with nitrogen containing less CO than generator gas.

A shifting of the equilibrium with temperature in the direction found indicates that the reaction from left to right is endothermic. In agreement with this, Fraenkel calculated the heat of this reaction to be ca. -243000 cals., and Richards¹¹⁴ -213220 cals. The reaction is, therefore, strongly endothermic.

As a result of a preliminary investigation of the influence of different forms of carbon and of various catalysts on the velocity of the reaction Fraenkel states, with all reserve, that different

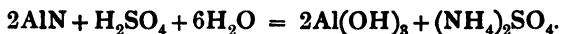
forms of carbon show essential differences in reaction-velocity, and that none of the catalysts so frequently mentioned in the Serpek patents show any marked influence on the reaction-velocity in the neighbourhood of 1500°.

The Badische Anilin-und Soda-Fabrik¹¹⁹ has also investigated the technical production of aluminium nitride. They find that the formation of nitride from alumina and coal is greatly accelerated by the presence of 5-10 per cent. of the oxides of certain elements which themselves can form stable nitrides. Under these conditions it is possible to secure rapidly and easily a fairly high percentage of nitrogen in the product. Among the oxides which may be used are those of Si, Ti, Zr, Mo, V, Be, Ce, Ur, Cr. Preference is given to SiO_2 on account of its cheapness, but under certain local conditions some of the others might be used with advantage, especially as they are recovered and can be used again. The oxides may be replaced by other oxygen compounds, such as silicates, titanates, vanadates, etc. The presence of iron and other impurities does not influence the catalytic action, so that low-grade bauxite may be employed.

The Badische¹²⁰ has also worked out methods of treating the crude nitride, so that, whilst the ammonia is completely recovered, the aluminium is obtained in the form of a pure compound. Thus by treating the crude aluminium nitride, containing, for example, silicon nitride, with limited amounts of acid or alkali, the aluminium may be obtained as a soluble compound, free from silica. The quantity

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of acid or base can also be chosen so that the aluminium remains as insoluble hydroxide, thus—



The elimination of ammonia by alkalies is greatly facilitated by the addition of such soluble salts as sodium chloride.

Production of Metallic Cyanides and Cyanamides.

The work of Defosses,¹²¹ Fownes,¹²² and Bunsen and Playfair¹²³ showed that by the action of nitrogen on a mixture of carbon and alkali or alkaline earth hydroxides or carbonates at high temperatures cyanides were formed, from which ammonia could be obtained. Several processes¹²⁴ based on these reactions were tried on a technical scale, but were abandoned on account of rapid deterioration of plant and high cost of production. Thus Margueritte and Sourdeval¹²⁵ used barium compounds instead of potassium compounds, as the former react much more readily with nitrogen. A mixture of N_2 and CO , obtained by passing air over glowing coal, was passed over a heated mixture of BaCO_3 , carbon, and iron. The $\text{Ba}(\text{CN})_2$ formed was treated with steam at ca. 300° , when NH_3 was liberated—



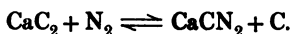
The $\text{Ba}(\text{OH})_2$ was used again in the formation of fresh cyanide. A somewhat similar process was carefully worked out by Mond,¹²⁶ but was also given up after trial, as it was found that NH_3 could be produced more cheaply by other methods.

Other processes aimed at the production of technically pure cyanides from atmospheric nitrogen. Castner¹²⁷ passed a mixture of nitrogen and hydrocarbons over a mixture of sodium and charcoal at a red heat and obtained NaCN. It was ultimately found more economical to substitute ammonia for nitrogen, and the method at present used by the Deutsche Gold-und Silberscheideanstalt for the manufacture of NaCN depends on this reaction.

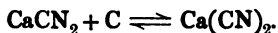
Cyanides and Cyanamides from Carbides.—In 1892 Moissan showed that calcium carbide, CaC_2 , could be prepared easily and in quantity in the electric furnace. The technical production of CaC_2 then developed rapidly, and in 1895 Frank and Caro¹²⁸ commenced their investigations on the absorption of nitrogen by metallic carbides, which have led to the establishment of the cyanamide industry on the present large scale. Moissan¹²⁹ showed that pure CaC_2 did not absorb nitrogen even at 1200° , but Frank and Caro found that technical carbides, such as BaC_2 and CaC_2 , absorbed nitrogen readily at much lower temperatures, probably owing to the impurities which they contain.

The metallic cyanamides are derivatives of cyanamide, H_2CN_2 , the constitutional formula of which is generally given as $\text{H}_2\text{N}\cdot\text{CN}$, although in some of its reactions it behaves as $\text{HN}=\text{C}=\text{NH}$, carbodiimide.¹³¹ The hydrogen is replaceable by metals giving the metallic cyanamides. By the action of nitrogen on metallic carbides, mixtures of metallic cyanides and cyanamides are obtained, the proportions depending on the metal and on the tempera-

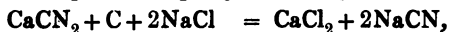
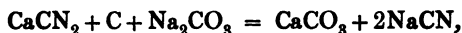
ture. The general type of the reaction may be illustrated by the case of CaC_2 . The formation of cyanamide takes place according to the equation—



Cyanide may then be formed as follows:—



With alkali carbides, cyanide preponderates largely in the equilibrium corresponding to the second equation. With BaC_2 about 30 per cent. cyanide and 70 per cent. cyanamide is obtained at 700° - 800° , whilst with CaC_2 cyanamide is practically the only product up to ca. 1100° . The equilibrium with SrC_2 lies between that of BaC_2 and CaC_2 . In all cases the proportion of cyanide increases with increasing temperature.^{128, 130, 132, 133} These facts explain the formation of cyanides by fusing the mixture of BaCN_2 or CaCN_2 and carbon with an alkali salt, such as the carbonates or chlorides of sodium and potassium—

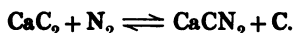


reactions which are used in the technical preparation of cyanides from CaCN_2 .

The Formation of Calcium Cyanamide from Calcium Carbide and Nitrogen.—From the technical point of view the action of nitrogen on CaC_2 is of the greatest importance, and although it has been the subject of numerous investigations, the exact nature of the reactions involved are not yet fully understood.

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The formation of CaCN_2 from CaC_2 and N_2 has usually been assumed to take place according to the reversible equation—

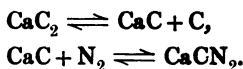


If CaC_2 , CaCN_2 , and C are regarded as separate solid phases, the system should be monovariant, and a definite equilibrium pressure of N_2 should correspond to a given temperature. The attempts to measure this equilibrium pressure led to very conflicting results. Matignon¹³⁴ calculated on theoretical grounds, under certain assumptions, that the pressure was 1 atmos. at ca. 1100°C . Caro¹³⁵ found an equilibrium pressure of 1 atmos. at 1360° for a certain specimen of technical carbide. Thompson and Lombard¹³⁶ investigated the equilibrium between 1050° and 1450°C ., and found that the equilibrium pressure varied rectilinearly with the temperature from ca. 2.5 cms. at 1050° to ca. 45 cms. at 1450° . By extrapolation, a temperature of ca. 1700° is obtained for an equilibrium pressure of 1 atmos. Their equilibrium pressures, however, involve an extraordinarily rapid variation of the heat of reaction with temperature, which makes it improbable that they represent true equilibria.¹³⁷ Le Blanc and Eschmann¹³⁸ were unable to get reproducible values of the nitrogen equilibrium pressure for a given temperature, and attribute this to sublimation of the CaCN_2 from hot to cold parts of the tube, where it is out of contact with carbon, and so cannot take part in the reverse reaction. Other possible disturbing factors are the gradual alteration of the

carbon, so that it becomes inactive, and the occurrence of side reactions, especially with impure carbide, the effects of which could not be taken into account. From their results it appears that the system is divariant, since the equilibrium pressure seems to depend not only on the temperature, but also on the concentration of nitrogen in the product. At 1300° this N_2 -concentration is about 85 per cent., and at 1200° about 90 per cent. of the theoretical. They assume that the CaC_2 - $CaCN_2$ mixture is a liquid phase, the other two phases necessary for a divariant system being solid carbon and the gas phase. The work of Erlwein, Warth, and Beutner¹³⁹ on the action of heat on CaC_2 threw a new light on the mechanism of cyanamide formation. They found that CaC_2 on heating decomposes into carbon and a lower carbide, which, although it does not react with water to give acetylene, is capable of absorbing nitrogen giving $CaCN_2$. A sample of technical carbide, containing 72 per cent. CaC_2 , gave only about 62 per cent. CaC_2 after heating for three hours at 500° - 1250° C., the CaC_2 -content being practically independent of the temperature. This does not, however, represent an equilibrium, as after thirty hours at 1000° only 36.6 per cent. CaC_2 remained. The addition of certain substances, especially of CaF_2 , greatly accelerates the decomposition. Thus the technical carbide with 10 per cent. CaF_2 contained only 27 per cent. CaC_2 after three hours at 1100° , and no CaC_2 after three hours at 1260° . The decomposition is especially rapid near the melting-point of CaF_2 (1330°). Bredig, Fraenkel, and Wilke¹³⁰ had already found a relation

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between the catalytic acceleration of cyanamide formation by salt additions and the melting-point of the added salt. These decomposed carbides can still absorb nitrogen, and the view is put forward that the subcarbide is probably an intermediate step in the formation of CaCN_2 from CaC_2 . If the subcarbide is assumed to be CaC , the formation of CaCN_2 would take place as follows: ¹³⁷—



For a proper understanding of the cyanamide equilibrium a thorough knowledge of the carbide dissociation is, therefore, required, and this is at present lacking. This may account for the failure hitherto to obtain concordant results.

The rate of absorption of nitrogen by CaC_2 alone, or with the addition of various substances, has been the subject of numerous investigations. Many of these have been prompted by the publication of patented processes, which claim that the addition of various substances to CaC_2 greatly accelerates the absorption of nitrogen, and allows it to take place at a lower temperature. The most important of these additions are CaCl_2 , proposed by Polzenius,¹⁴⁰ and CaF_2 , proposed by Carlson.¹⁴¹ Various explanations of the action of these salts have been put forward in the patent literature and elsewhere.¹⁴² These explanatory hypotheses have been tested by Bredig, Fraenkel, and Wilke.¹⁴³ They heated powdered carbide (81.5 per cent. CaC_2), with or without the addition of 10 per cent. of other substances, for two hours in

a nitrogen atmosphere, and determined the amount of nitrogen absorbed. At 800° CaC_2 alone absorbed ca. 3 per cent. N_2 ; CaC_2 with 10 per cent. CaCl_2 absorbed 22 per cent. N_2 ; with 10 per cent. BaCl_2 , 12.5 per cent. N_2 ; with 10 per cent. LiCl , NaCl , and KCl , 17 per cent., 12 per cent., and 11 per cent. N_2 respectively. It appears, therefore, that with the chlorides of metals of the same group of the periodic system the acceleration is greater the lower the atomic weight of the metal. This was confirmed with the chlorides of Be, Mg, and Sr. On the other hand, the quantity of cyanide in the product increases with the atomic weight of the metal, but at the temperatures employed is always very small with CaC_2 . Addition of 10 per cent. CaF_2 , CaSO_4 , CaO , $\text{Ca}(\text{OH})_2$, MgO , coke-powder, and sand caused little or no acceleration at 800° . Similar results were obtained at 700° , but LiCl gave a greater acceleration than CaCl_2 . With CaC_2 alone the absorption begins at 750° , whilst the mixtures with NaCl and CaCl_2 begin to absorb at 650° . At 800° the initial velocity of absorption is very rapid with NaCl and KCl , but falls off much more quickly than with CaCl_2 . Metallic Ca, Mg, and Na do not appreciably accelerate the velocity of absorption. From these results Bredig, Fraenkel, and Wilke exclude the following hypotheses: (1) that the real catalysers are oxysalts, since CaO cannot replace CaCl_2 in efficiency; (2) that the added salt causes only a considerable initial rise of temperature, since CaCl_2 shows marked catalytic effect although the temperature is kept constant; (3) that the addition serves only to make the mass

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more porous, since sand, MgO , and charcoal have practically no influence; (4) that the addition gives rise to dissociation products, such as Ca , which facilitate the reaction, possibly by intermediate reactions, since the addition of metallic Ca has no effect.

The other explanation is that the addition acts as a solvent in which the reaction between CaC_2 and N_2 goes faster than with solid CaC_2 . The flux also keeps the surface of the carbide free from lime and from reaction products. Bredig, Fraenkel, and Wilke support the view that the acceleration is connected with the fusibility of the added salt, and the solubility of CaC_2 in the flux. The melting-point of the salt is not, however, the only factor. The acceleration will depend on the complete melting-point diagram of the complex reaction mixture, on the solubility of CaC_2 in the melt, and on the specific velocity-constant for the particular melt. They found, further, that the velocity of absorption of nitrogen is proportional to the pressure in the interval investigated (up to 1 atmos.). Rudolphi¹⁴⁴ obtained similar results with CaCl_2 , and concluded that the influence of the added salt is directly connected with its melting-point, but he could not settle the exact mode of action of the fused salt. He further showed that the formation of CaCN_2 from CaO , C , and N_2 begins between 1738° and 1753° , and that the formation of CaC_2 precedes that of CaCN_2 , since the product contains either both CaC_2 and CaCN_2 or neither, according as the temperature is above or below 1738° - 1753° .

Foerster and Jacoby¹⁴⁵ found, in agreement with

Frank and Caro, that powdered commercial carbide (containing ca. 10 per cent. $\text{Ca}(\text{OH})_2$) does not show rapid absorption of nitrogen below 1000° . At 1050° - 1100° the absorption was rapid and complete. At lower temperatures not only is the absorption less rapid, but it is also incomplete. The amount absorbed tends to a limiting value below the theoretically possible, and the limiting value is lower the lower the temperature. That we are not dealing here with an equilibrium is shown by the fact that the exothermic reaction is favoured by rise of temperature. A completely azotised product, prepared at 1100° , also showed no diminution of N_2 -content when heated four hours at 900° . With CaC_2 containing CaCl_2 or CaF_2 the results are different; the absorption is much more rapid than with CaC_2 alone, and does not cease at a limiting value, but increases regularly with the time of heating. Thus CaC_2 with 15 per cent. CaCl_2 absorbed seven times as much N_2 in two hours at 700° as did CaC_2 alone at 800° . CaF_2 requires a higher temperature than CaCl_2 to show the same effect. Thus with 10 per cent. CaF_2 the absorption of N_2 in two hours at 900° was the same as with 15 per cent. CaCl_2 at 800° . The effect of the quantity of catalyst added is peculiar. With increasing quantities of CaCl_2 the N_2 -absorption in two hours increases rapidly at first, and then more slowly, until with 30 per cent. CaCl_2 almost complete azotisation is obtained. With CaF_2 the N_2 -absorption in two hours rises rapidly to a maximum with increasing percentage of CaF_2 , and then falls on further addition. At 800° the maximum absorption

in two hours (8 per cent. N_2) is obtained with 5 per cent. CaF_2 , and at 900° with 3 per cent. CaF_2 (29 per cent. N_2). The behaviour of CaC_2 alone, compared with that of a mixture with $CaCl_2$ or CaF_2 , seems to show that the influence of the addition is to remove some resistance to the continued N_2 -absorption. Foerster and Jacoby assume that the resistance is due to protecting layers of reaction products on the carbide, and that the liquefaction or softening of a portion of the reaction-mass by the $CaCl_2$, the melting-point of which is below 800° , prevents the existence of these protecting layers, and explains its favourable action. The difference in the behaviour of pure and technical CaC_2 is similarly explained by the presence of CaO in the latter. This is known to lower the melting-point of CaC_2 , and an incipient softening of the mass at 1100° might well explain the absorption of nitrogen by technical carbide. It also explains why further addition of CaO has no considerable effect, and why the addition of substances which only increase the porosity of the mass, but which cannot effect liquefaction, do not help absorption. Besides dissolving protecting layers, liquefaction of the mass allows nitrogen to dissolve, and thus increases the velocity of its action. These results might be considered of importance technically, as the lower reaction-temperature caused by salt additions means a saving of fuel and less wear of the reaction-chambers. It is maintained, however, from the technical side,¹⁴⁶ that even though the temperature of active absorption is lowered by these salts, this is not of much importance technically, as with

large masses the great heat liberated by the reaction would raise the temperature to that usually employed without additions.

In a later investigation Foerster and Jacoby¹³³ found that the influence of different quantities of CaF_2 is practically the same after long heating, and that even in presence of CaF_2 at $800^\circ\text{--}860^\circ$ the nitrogen absorption is limited. The limiting value for a given temperature is independent of the percentage of CaF_2 (up to 10 per cent.), which determines, however, the velocity with which the saturation-point is reached. They assume that at these temperatures the CaF_2 is unable to remove the whole of the protecting layer from the CaC_2 . CaCl_2 has a much greater solvent action, corresponding to its lower melting-point. They agree with Bredig, Fraenkel, and Wilke, however, that the action does not depend on the melting-point of the added salt alone, but on the whole complicated melting-point diagram of the system. They also found that the velocity of nitrogen absorption by $\text{CaC}_2\text{--CaF}_2$ mixtures was proportional to the pressure.

Pollacci¹⁴⁷ found that K_2CO_3 had a marked accelerating effect. The temperature of absorption depends on the percentage of K_2CO_3 . At 900° the absorption is a maximum with 4 per cent. K_2CO_3 . Pollacci regards the effect of K_2CO_3 as purely catalytic and not due to liquefaction phenomena. As regards the influence of pressure, he found that increase of pressure does not lower the temperature of absorption, but increases the velocity of absorption up to 2 atmos. Increase of pressure above this

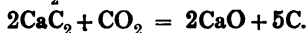
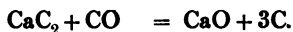
amount makes little difference to the velocity of absorption.

Technical production of Calcium Cyanamide. ^{71, 123, 143}

—Several modifications of the original Frank-Caro process for the manufacture of CaCN_2 by the action of nitrogen on CaC_2 have been from time to time proposed. These modifications consisted in the addition to the CaC_2 of various substances which accelerate the absorption of nitrogen. Of these the most important depend on the addition of CaCl_2 (Polzenius) or of CaF_2 (Carlson). The latter does not seem to have been worked technically. The Polzenius method, in which 10 per cent. CaCl_2 was added to the CaC_2 , was started at Westeregeln in 1906. In 1908 it came under the control of the Cyanidgesellschaft, which controls the Frank-Caro patents, and was discontinued in 1910, as experience showed that the Frank-Caro process was the more economical.

For a time, owing to the high price of carbide, CaCN_2 was manufactured from lime, carbon (coal), and nitrogen. The product, however, contained only ca. 12 per cent. N_2 , compared with ca. 20 per cent. in the product from carbide, and when the price of carbide dropped again a return was made to the original process.

The nitrogen employed must be as free as possible from moisture, O_2 , CO , and CO_2 . These act either on the carbide or on the cyanamide, and diminish the percentage of nitrogen in the final product. Thus, CO and CO_2 decompose CaC_2 as follows:—



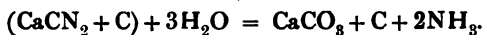
Not only do they react with CaC_2 , but also with CaCN_2 . The percentage of nitrogen rapidly diminishes when a current of CO or CO_2 is passed over heated CaCN_2 . In a few factories the nitrogen is prepared by passing air over heated copper turnings, the copper oxide formed being subsequently reduced by heating in a current of reducing gases. More commonly the nitrogen is prepared by the fractional distillation of liquefied air by the Linde or Claude apparatus, which give dry nitrogen containing less than 0.4 per cent. oxygen.

The earlier furnaces were externally heated closed retorts, connected with the nitrogen supply and provided with charging and discharging arrangements. Their great disadvantage was the difficulty of regulating the temperature. The reaction is strongly exothermic, and the temperature rose so high that the walls of the furnace rapidly deteriorated, and the product often set to an extremely hard mass on the furnace walls and could be removed only with difficulty. As at present carried out in the most up-to-date factories, such as that of the North-western Cyanamide Company at Odda, Norway, the carbide is finely ground in an air-tight apparatus and filled into drum-shaped retorts, which hold from 300 to 500 kilos. These retorts consist of a sheet-iron cylinder, perforated to allow passage of the nitrogen, and lined externally with refractory material. Down the centre of the retort passes a thin carbon rod, contained in a cardboard tube to separate it from the carbide. The rod is used as a heating resistance.

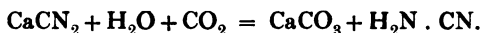
After filling the retort the lid is fixed on air-tight. A number of these retorts are then placed in a long horizontal chamber, the terminals of each carbon rod connected to the current supply, and the chamber closed air-tight. The air is displaced by nitrogen and the current turned on, the connection with the nitrogen supply being maintained. The nitrogen is admitted at a pressure slightly above atmospheric, so as to prevent access of air. The temperature in the neighbourhood of the resistor rises to about 1000° , and the reaction starts from the centre and proceeds outwards. The current is kept on until a certain proportion of the mass has reacted, when the exothermic reaction is able to proceed to completion without further application of heat. The end of the absorption is indicated by a gas-meter on the nitrogen supply. The whole time of absorption is from thirty to forty hours. The drums are then withdrawn and allowed to cool for eight to twelve hours. The black, sintered mass, which occupies a smaller volume than the original carbide, is then removed, ground and packed in sacks. The crude cyanamide contains from 20-22 per cent. N_2 , corresponding to 57-63 per cent. $CaCN_2$. It contains in addition about 20 per cent. lime, 7-8 per cent. silica, iron oxide, and alumina, and 14 per cent. carbon in the form of graphite. Various trade names have been given to it—"Kalkstickstoff," "Stickstoffkalk," "lime nitrogen," "nitrogen lime"—but in this country it is usually known as "nitrolim."

Uses of Nitrolim.—The most important property of $CaCN_2$ is the ease with which it gives up the

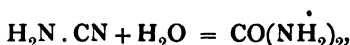
whole of its nitrogen as ammonia when treated with superheated steam or water under pressure—



The NH_3 is absorbed by H_2SO_4 , giving pure $(\text{NH}_4)_2\text{SO}_4$. The residual $\text{CaCO}_3 + \text{C}$ may be employed again for the manufacture of CaCN_2 . When CaCN_2 is used as a manure it undergoes a complex decomposition, the ultimate products being ammonium compounds. The chief reactions are probably the following. By the action of moisture and CO_2 in the soil cyanamide is formed—



This is then converted into urea—



and finally into ammonium carbonate—



Bacteria play an important part in the process. For the advantages and disadvantages of nitrolim as a fertiliser, reference must be made to the numerous articles in the various agricultural journals.

By extracting technical calcium cyanamide with hot water, dicyandiamide is easily obtained pure in crystalline form—

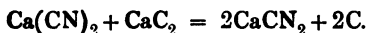


The compound is used in the preparation of organic dyes and as a substitute for ammonium oxalate for lowering the temperature of combustion

of explosives. Various other substances, such as urea, guanidine, nitroguanidine, and creatin may be prepared from calcium cyanamide, and it also forms the basis of "ferrodur," which is used in place of ferrocyanides for the case-hardening and tempering of iron and steel.

Clancy¹⁴⁹ describes a process for the extraction of gold from its ores, in which cyanides are wholly or partly replaced by calcium cyanamide.

Cyanides from Nitrolim.^{128, 148} — The theory of the transformation of cyanamide to cyanide has already been discussed (p. 88). In practice the crude ($\text{CaCN}_2 + \text{C}$) mixture is fused with common salt, when 90-95 per cent. of the cyanamide is converted into cyanide. The product contains about 30 per cent. NaCN and can be used directly for gold extraction, or it may be converted into pure cyanide by decomposing it with acids and absorbing the liberated HCN by caustic alkalies. The formation of cyanide from cyanamide is a reversible reaction, and special provision has to be made to prevent re-formation of cyanamide after complete fusion. Further, at the temperature of fusion there may be a decomposition of CaCN_2 giving CaC_2 , which can act on cyanide as follows :—



By using appropriate appliances for melting and cooling the materials, these difficulties have been overcome and the conversion of cyanamide into cyanide is practically quantitative.

Factories for the manufacture of cyanamide are

in operation in France, Germany, Norway, Italy, Hungary, Switzerland, the United States, and Japan.¹⁵³ No process of any kind for the fixation of atmospheric nitrogen has yet been established in Britain.

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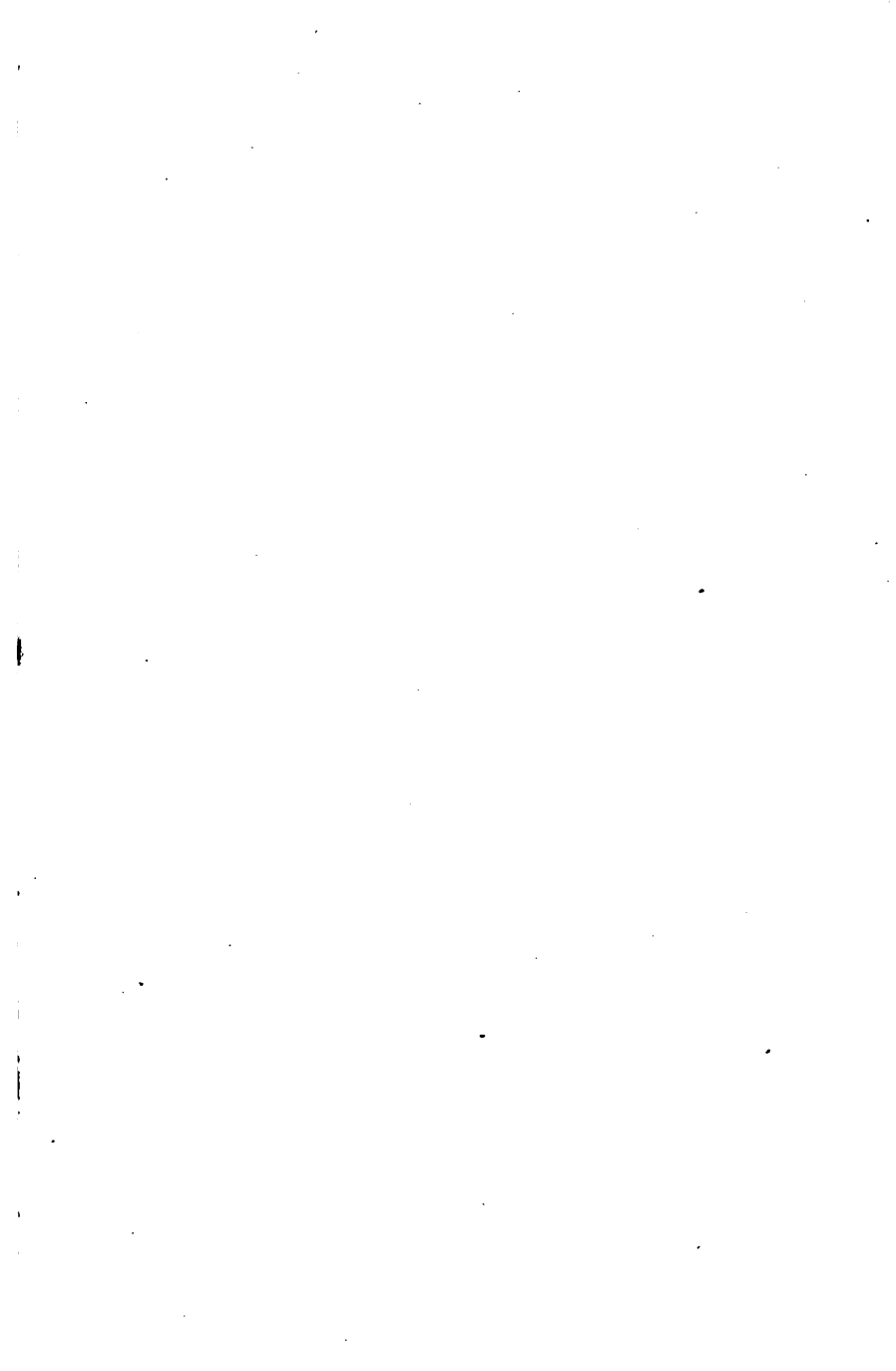
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